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USING LIFE CYCLE ASSESSMENT (LCA) TO EVALUATE THE ENVIRONMENTAL CHARACTERISTICS OF ETHANOL BIOREFINERY

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Ce mémoire intitulé :

USING LIFE CYCLE ASSESSMENT (LCA) TO EVALUATE THE ENVIRONMENTAL CHARACTERISTICS OF ETHANOL BIOREFINERY

présenté par : RANJBAR Mahasta

en vue de l'obtention du diplôme de : Maîtrise ès sciences appliquées

a été dûment accepté par le jury d'examen constitué de :

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To my parents for their love, endless support

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Résumé

La dépendance au pétrole est perçue par chaque pays comme un risque majeur pour le secteur énergétique. Récemment, afin de réduire ce risque, la production de l'éthanol à partir de biomasses renouvelables a reçu une attention particulière, même si l'éthanol est utilisé comme combustible depuis 1908. L'éthanol comme source d'énergie renouvelable présente de nombreux avantages environnementaux dont le plus évident est la réduction des émissions de dioxyde de carbone permettant de diminuer les risques potentiels associés au changement du climat. Beaucoup d'experts voient cette opportunité comme une alternative de notre dépendance aux sources d'énergie non renouvelables.

La capacité à produire de l'éthanol à partir de biomasse cellulosique à bas coût est la clé pour rendre l'éthanol compétitif par rapport à l'essence. Mais le choix de source de biomasse joue un rôle important en terme de performance environnementale pour la production de l'éthanol. De nos jours, des pays comme le Brésil et les États-Unis s'intéressent au potentiel énorme que peut offrir l'éthanol. Aux États-Unis, l'éthanol est produit à partir du maïs, alors que le Brésil utilise la canne à sucre pour ce faire. Passer de ces produits, principalement cultivés pour la chaîne agro-alimentaire, à des cultures destinées à produire de l'énergie peut présenter des avantages environnementaux et une efficacité énergétique plus accrus que les cultures vivrières pour l'éthanol. Comme la conversion de diverses matières premières en éthanol est associée à plusieurs coproduits et à des activités aratoires, il n'est pas évident de déterminer la méthodologie qui pourrait analyser de façon appropriée la performance environnementale de la production d'éthanol.

L'analyse de cycle de vie (ACV) est reconnue comme une approche systématique et pratique pour implanter le concept de la pensée cycle de vie dans une perspective durable. En tenant compte de toutes les étapes du cycle de vie du produit, l'ACV est capable d'incorporer les facteurs environnementaux dans la phase de conception préliminaire afin de comparer les options de conception et d'améliorer l'identification des options pouvant être les plus bénéfiques pour l'environnement considérant les matières premières utilisées, les méthodes du procédé de fabrication et les stratégies de recyclage. Selon les standards ISO, l'ACV comporte quatre étapes qui sont : 1) définition de l'objectif et de l'envergure des travaux, 2) inventaire du cycle de vie (LCI), 3) évaluation d'impact (LCIA) et 4) interprétation. Cependant, à chaque étape, des

méthodologies différentes doivent être sélectionnées avec soin afin d'obtenir une évaluation appropriée de la production d'éthanol. Il est évident qu'il n'existe pas de façon unique de choisir la méthodologie la mieux appropriée pour une ACV de l'éthanol, et cela représente un défi pour les analystes d'ACV. Il n'en demeure pas moins qu'il faut considérer les impacts de ces divers choix sur les résultats.

Dans ce contexte, le principal objectif de ce projet est d'identifier les paramètres environnementaux adéquats pour une application ACV qui pourraient être utilisés pour évaluer le bioraffinage de l'éthanol, avec une emphase sur l'évaluation de coproduits associés à différentes matières premières.

Pour rencontrer l'objectif décrit ci-dessus, un cadre de travail ACV a été construit sur l'évaluation des connaissances liées à diverses études ACV réalisées pour l'éthanol. Cette évaluation a été conduite afin d'identifier les choix méthodologiques selon leur importance et leur impact sur le résultat final. Vingt-six (26) études ACV concernant la production d'éthanol à partir de diverses matières premières ont été considérées. Une revue critique des forces et des faiblesses de différentes approches a été réalisée afin de déterminer l'impact sur les résultats des diverses méthodologies sélectionnées. L'étude a comparé les résultats obtenus et les conséquences des différents choix méthodologiques concernant les limites du système, les procédures d'attribution des ressources et les catégories d'impact environnemental. Pour évaluer l'impact des différents choix méthodologiques dans une ACV, un cas de base a été défini afin d'appliquer et de comparer les différents choix méthodologiques, d'évaluer leurs conséquences et de proposer une méthodologie alternative pour les évaluations d'études de cas pour la production d'éthanol.

C'est pourquoi une étude ACV de production d'éthanol à partir de copeaux a été sélectionnée comme cas de base afin de caractériser les choix méthodologiques. Les résultats montrent que dans ce cas spécifique quand l'éthanol sert de combustible, 'du berceau à la porte' représente une définition approprié de la limite du système afin d'éviter des activités supplémentaires dans le système. Cela offre également l'opportunité de comparer la production de l'éthanol réalisée à partir de diverses matières premières et d'identifier les points chauds du système. En termes de catégories d'impact environnemental, la sélection des valeurs médianes semble plus pertinente, à cause des plus grandes incertitudes à ce niveau. La méthode d'allocation peut avoir une forte influence sur les résultats selon les paramètres clés mentionnés. Dans le cas copeaux-à-éthanol avec l'électricité comme coproduit, le meilleur choix est d'éviter l'allocation par expansion du système. Ceci permet d'inclure toutes les activités reliées à la fois à la production d'éthanol et d'électricité.

Après avoir identifié la méthodologie la mieux appropriée pour une application ACV, quelques scénarios ont été identifiés pour comparer les avantages et les désavantages environnementaux de la production d'éthanol à partir de différentes sources de biomasse cellulosique. Ces scénarios incluent la production d'éthanol à partir de copeaux de bois, de cultures énergétiques (triticale) et d'hémicelluloses. Ces matières premières peuvent être utilisées pour produire seulement de l'éthanol ou comme base pour le concept de bioraffinerie forestière intégrée (IFBR) dans une usine papetière. Cette industrie représente un secteur important de l'économie canadienne et tend à améliorer constamment sa performance environnementale du point de vue cycle de vie. En effet, l'application d'ACV dans les analyses de procédés se s'est multipliée ces dernières années et il existe un potentiel pour l'utilisation d'ACV dans l'analyse des variantes de procédés, c'est-à-dire l'analyse d'impacts de la modification dans l'usine sur la performance de tout le système. Dans cette étude, deux concepts IFBR sont étudiés. L'un est l'utilisation novatrice de deux procédés, le premier fournissant de l'éthanol (produit principal) et de l'énergie (coproduit) sous forme de vapeur. Cette vapeur est ensuite envoyée à l'usine de pâte afin de fournir l'énergie additionnelle requise pour la mise en pâte en changeant le type de générateur utilisé dans l'usine d'éthanol. L'autre concept inclut l'extraction des hémicelluloses du bois avant la mise en pâte et leur conversion en éthanol, tout en utilisant les matériaux résiduels pour fabriquer de la pâte Kraft. Deux autres scenarios considèrent l'utilisation de copeaux de bois et du triticale pour produire de l'éthanol dans un contexte *Greenfield*. Le triticale, culture énergétique, est un croisement entre le blé et le seigle largement implanté dans l'ouest canadien.

Ces scénarios ont été utilisés pour illustrer la méthodologie ACV proposée: 1) identification des paramètres environnementaux pertinents pour la production d'éthanol, 2) identification des aspects et suivi de la performance environnementale de divers scenarios pour le bioraffinage de l'éthanol à l'aide de divers paramètres environnementaux. Ces scénarios ont démontré que:

- Le développement de paramètres qui relient la performance environnementale aux procédés de production est un excellent moyen d'intégrer l'objectif de durabilité à la prise de décision.

- Les paramètres environnementaux classiques, utilisés pour des études spécifiques, qui ne sont pas adéquats pour sélectionner des options environnementales de bioraffinage de l'éthanol, devraient être améliorées à l'aide de paramètres appropriés.
- Les paramètres d'analyse de sensibilité et de scénarios doivent être sélectionnés afin d'obtenir une meilleure compréhension des impacts sur les résultats.

En conclusion, la sélection des meilleurs choix méthodologiques obtenus grâce au modèle de référence permet de définir la méthodologie ACV appropriée afin de procéder à une évaluation environnementale de la production d'éthanol. Cette méthodologie est ensuite utilisée dans différents scénarios pour identifier les opportunités environnementales de chacun d'entre eux.

Abstract

The dependence on oil is a major risk factor when considering the energy security in each country. Recently, in order to mitigate this risk, the production of ethanol from alternative, renewable resources has received special attention although it has been used as a fuel since 1908. Ethanol as a renewable and biodegradable source of energy undoubtedly provides numerous environmental benefits. The most obvious is an increased saving in carbon dioxide emissions which results in a reduction of the potential risks associated with climate change. Furthermore, many see this as an opportunity to shift away from the reliance on non-renewable energy sources.

The ability to produce ethanol from cellulosic biomass at a low cost is the key to making ethanol competitive with gasoline. However, choosing the biomass source plays an important role in terms of the environmental performance of ethanol production. At present, countries such as Brazil and the United States are tapping into the enormous potential ethanol has to offer. In the United States, ethanol is produced using corn, while in Brazil, sugarcane is used. Shifting from these crops that are mainly grown for food or feed usage to crops grown for fuel usage can significantly improve the environmental benefits and energy efficiency. As the conversion of different feedstocks to ethanol is associated with various co-products and tillage activities, it is not obvious which methodological framework can analyse the environmental performance of ethanol production appropriately.

Life cycle assessment (LCA) is recognized as a systematic and practical approach to the implementation of the life-cycle thinking concept in sustainable design. By taking into consideration all stages of the product life cycle, LCA is capable of incorporating environmental factors into the early design phase in order to compare design options and to improve the identification of the, potentially, most environmentally beneficial options by considering raw material use, the manufacturing process and recycling strategies. According to the ISO standard, LCA has four steps including: 1) goal and scope definition, 2) inventory (LCI), 3) impact assessment (LCIA) and 4) interpretation. However, in each step, different methodological choices need to be made carefully in order to obtain an appropriate evaluation of ethanol production. Generally, the methodological choices are key points for an ethanol LCA study and there are many trade-offs when selecting the most appropriate methodology for an ethanol LCA.

These different choices pose a challenge for LCA analyzers. It is obvious that there is no single way to make these choices but it is important to consider the consequences they may have on the results.

In this context, the main objective of this project is to identify suitable LCA-based environmental metrics which can be used to assess the ethanol biorefinery, with emphasis on evaluating the co-products associated with different feedstocks.

To meet the above objective, an LCA framework was built based on the assessment of a body of knowledge related to ethanol LCA studies. This assessment was done in order to identify some of the methodological choices according to their significance and their consequences for the final result. It focused on a survey of 26 LCA studies concerning the production of ethanol from different feedstocks. A critical review of the strengths and weaknesses of the different approaches was done to determine the impact of different methodological choices on the results. The review compared the results and consequences of each of the methodological choices which included choices such as the system boundaries, allocation procedures and environmental impact categories. To assess the impact of different methodological choices in an LCA, a base case was defined for application and comparison of these choices in order to assess their consequences and propose an alternative methodology for ethanol production assessments.

For this reason, an LCA study for production of ethanol from woodchips was selected as a base case in order to characterize the methodological choices. The results show that for this specific case, when ethanol is assumed as fuel, cradle-to-gate is an appropriate system boundary to avoid the extra activities in the system. It also gives the opportunity to compare ethanol production from different feedstocks and identify the hot-spots in the system. In terms of environmental impact category, selection of midpoint seems to be more appropriate because of more certainties in this level. The allocation method can have a strong influence on the results among the mentioned key points. In the case of woodchips-to-ethanol producing electricity as a co-product, the best selection is avoiding allocation by system expansion. It enables to include all activities related to both ethanol and electricity production.

After identifying the most appropriate LCA-based methodology, several scenarios were identified for the comparison of environmental advantages and disadvantages of ethanol production from different cellulosic biomass feedstocks. These scenarios included ethanol production from wood chips, an energy crop (triticale) and hemicellulose. These feedstocks can be used in greenfield ethanol production or at an Integrated Forest Biorefineries (IFBR) at an existing pulp and paper mill. The pulp and paper industry is an important Canadian industrial sector with many motivations for continuously improving its environmental performance from a life cycle perspective. Therefore, the application of LCA in pulp and paper process analysis has increased in recent years and there is a potential of using LCA in the assessment of process variants, in order to analyze the effect of mill modifications on the performance of the whole system. In this study two aspects of the IFBR were studied. One process is a novel use of two processes, the first of which provides ethanol (main product) and energy (co-product) in the form of steam. This steam is then sent to the pulp mill in order to provide the additional energy required for the pulping by changing the type of generator used in the ethanol mill. The other aspect includes the extraction of hemicellulose from wood prior to pulping and converting it into ethanol, while using the remaining wood components to produce Kraft pulp. Two other scenarios include woodchips and triticale for greenfield ethanol production. Triticale which is a man-made crop developed by crossing wheat with rye, is grown widely in western Canada.

These scenarios were used to illustrate the proposed LCA methodology: 1) identification of relevant environmental metrics for ethanol production, 2) identification of aspects and monitoring the environmental performance of different scenarios for an ethanol biorefinery by utilizing these environmental metrics. These scenarios demonstrated that:

- The development of metrics that quantify the environmental performance of production processes is an excellent way to integrate the goal of sustainability into decision-making.
- Classical environmental metrics used for specific studies which are not by themselves adequate for selecting environmentally preferred ethanol Biorefinery options, should be enhanced by other appropriate metrics.
- The sensitivity and scenario analysis parameters need to be selected in order to have a better understanding of the consequences on the results.

  In conclusion, the selection of the best methodological choices obtained according to the baseline model identifies the appropriate LCA methodology to make for the environmental evaluation of ethanol production. This methodology is then used in different scenarios to identify environmental opportunities for each of them.

Condensé en français

Introduction

L’éthanol étant renouvelable et biodégradable, son utilisation comme source d’énergie présente de nombreux avantages environnementaux dont le plus évident est une réduction plus importante des émissions de dioxide de carbone et par conséquent une diminution des risques potentiels reliés au changement du climat. De plus, l’éthanol est perçu comme une opportunité de se libérer de la dépendance aux sources d’énergie non renouvelables. Il peut être produit à partir de biomasse contenant du sucre, d’amidon et de cellulose. Jusqu’à présent, les matières premières renfermant du sucre et de l’amidon ont été les principales sources pour produire de l’éthanol. Cependant la compétition qu’elles rencontrent face à la demande agro-alimentaire qui a une incidence sur les prix risque de limiter l’expansion de la première génération de production d’éthanol. Comme la conversion de la biomasse cellulosique en éthanol offre potentiellement beaucoup d’avantages, la recherche devrait améliorer la performance environnementale ainsi que les aspects socio-économiques afin d’assurer un avenir durable à la seconde génération de production d’éthanol. Les matières premières produisant de la biomasse cellulosique sont en général largement répandues et en abondance. De plus, elles ne présentent pas d’intérêt pour la filière agro-alimentaire. Enfin, la production d’éthanol de seconde génération à partir des matières premières du Canada présente un potentiel énorme.

Les cultures énergétiques, en particulier le triticale, sont de nouvelles matières premières pour la production de l’éthanol au Canada. Le triticale est une céréale artificielle développée par l'homme grâce au croisement de la culture du blé et du seigle. L'Initiative Canadienne de Bioraffinage du Triticale (ICBT) est un programme de recherche et développement sur 10 ans, pour développer le triticale comme culture pour le bioraffinage industriel au Canada. Le réseau ICBT a pour objectif de développer de nouvelles façons d'utiliser le triticale comme une biomasse pour la production d'éthanol et la fabrication de biomatériaux.

Au Canada, les copeaux de bois représentent une autre biomasse potentielle. L'utilisation de cette biomasse pour la production d'éthanol augmente les chances de pouvoir intégrer la production d'éthanol dans une usine de pâtes et papiers. L’industrie papetière canadienne est un important gestionnaire de biomasse et par conséquent elle peut cibler la production d’éthanol cellulosique. Ceci signifie que l'industrie papetière a un grand rôle à jouer dans le développement de la production d'éthanol de seconde génération, d'autant plus qu'elle a pour objectif une amélioration continue de l'environnement.

Dans ce contexte, les outils d'intégration de processus peuvent servir à évaluer systématiquement de nouveaux procédés pour le bioraffinage de l'éthanol. L'analyse de cycle de vie (ACV) est un outil pour évaluer les impacts environnementaux potentiels ainsi que les ressources utilisées tout au long du cycle de vie de l'éthanol, en partant des matières premières jusqu'à la disposition finale et la gestion des déchets. L'ACV de la production d'éthanol peut également permettre d'identifier des améliorations possibles. L'ACV comporte quatre étapes qui incluent la définition de l'objectif et la portée, l'analyse de l'inventaire du cycle de vie (ICV), l'Évaluation de l'impact du cycle de vie (ÉICV) et l'interprétation. La définition de l'objectif et la portée campent les raisons pour lesquelles l'étude est réalisée. Les limites du système et l'unité fonctionnelle doivent être définies à cette étape. Toutes les entrées et sorties du cycle de vie du produit sont déterminées lors de l'analyse ICV. Le but de l'ÉICV est de comprendre et d'évaluer les impacts du système sur l'environnement. Par la suite, lors de l'étape d'interprétation, les résultats sont évalués par rapport à l'objectif et à l'envergure. Diverses méthodologies doivent être choisies lors d'une ACV. Le choix des meilleures méthodologies disponibles est nécessaire afin d'améliorer l'évaluation environnementale de la production d'éthanol à partir de diverses biomasses.

Dans le cadre du bioraffinage de l'éthanol, il y a de nombreuses possibilités pour déterminer la performance environnementale. Différentes combinaisons de la procédure d'allocation, les limites du système étudié et les indicateurs utilisés pour l'évaluation environnementale produisent des résultats divergents pour l'ACV de l'éthanol. Ces divergences se produisent parce qu'il n'existe pas de façon unique pour faire des choix de méthodologies afin de réaliser une évaluation ACV de l'éthanol.

Ce manque dans l'ensemble des connaissances est la force motrice de cette étude afin de proposer une méthodologie pertinente basée sur l'ACV pour l'évaluation environnementale de divers procédés de bioraffinage de l'éthanol.

La principale hypothèse de ces travaux est :

Différents procédés de bioraffinage de l'éthanol pour fabriquer des produits et des coproduits sont préférables pour l'environnement sous des conditions spécifiques de design qui peuvent être déterminées à l'aide d'un processus d'évaluation ACV systématique et des paramètres appropriés.

Les objectifs de cette étude sont les suivants:

- Évaluer l'ensemble des connaissances liées à des études ACV pour la production de l'éthanol à partir de diverses biomasses, afin de comprendre les approches basées sur l'ACV utilisées pour l'attribution des charges environnementales en vue d'évaluer les alternatives de conception pour le bioraffinage de l'éthanol.
- Identifier un ensemble de paramètres qui cernent les caractéristiques environnementales les plus importantes du procédé de bioraffinage afin de quantifier l'impact de la production de l'éthanol sur l'environnement,
- Appliquer une méthodologie ACV qui convienne le mieux pour comparer les impacts environnementaux des divers scénarios de production d'éthanol à partir de diverses biomasses en calculant et en interprétant un ensemble d'impacts environnementaux dans le cadre d'une étude de cas.

Méthodologie

Une méthodologie doit être développée afin de définir le problème et d'établir l'hypothèse afin de démontrer les avantages d'utiliser un cadre ACV. L'approche générale de l'étude est illustrée en figure 1.

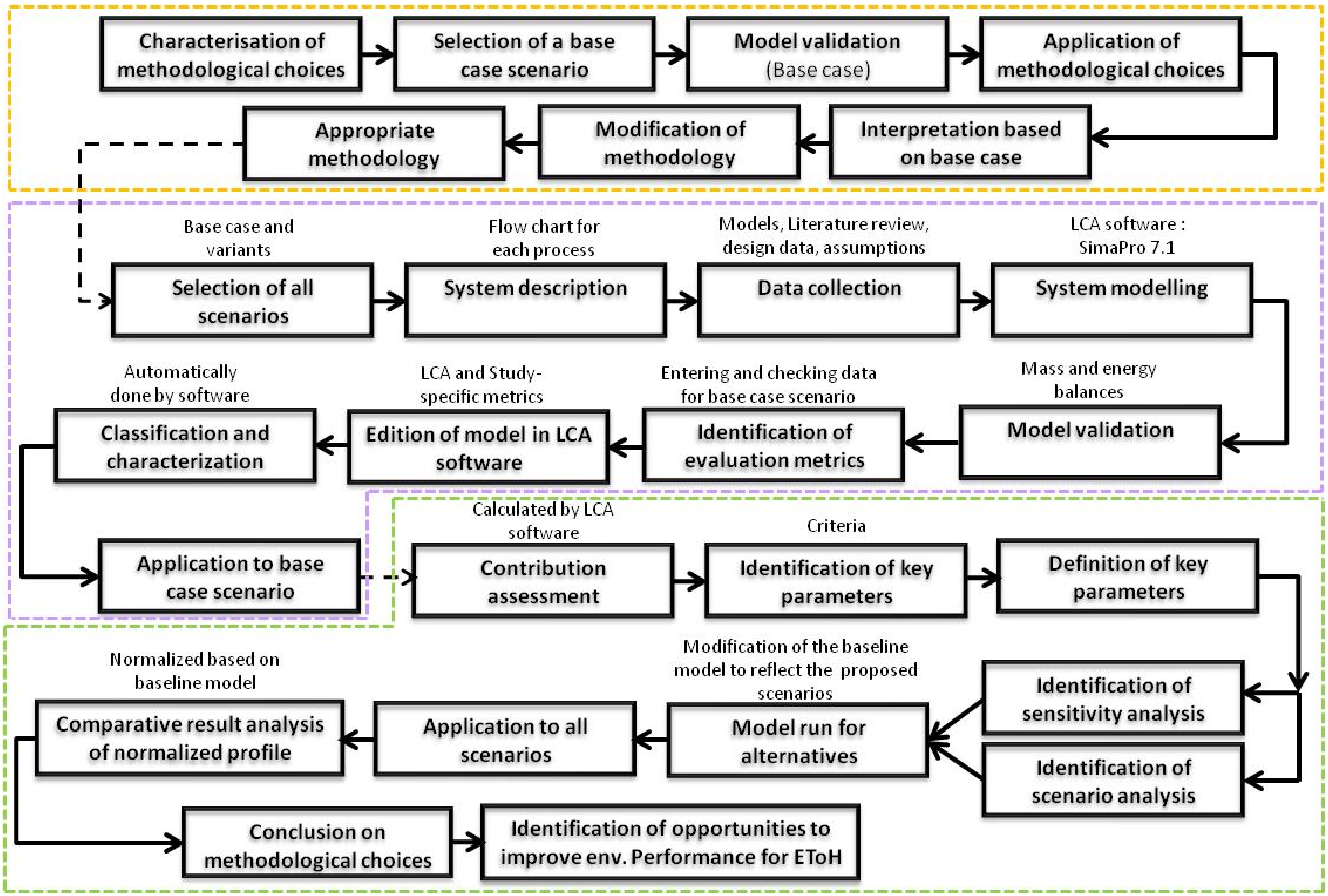

Figure1. Approche générale de l'étude

La méthodologie générale de ces travaux comprend trois blocs.

1. Caractérisation et exploration de choix de méthodologies

Le premier bloc identifie les choix méthodologiques, tels que les limites du système, le type d'impact environnemental et la procédure d'allocation, qui ont été faits dans les études ACV de l'éthanol. Les conséquences de ces choix pour la production d'éthanol sont évaluées afin de proposer une méthodologie ACV appropriée. Vingt-six (26) études ACV concernant la production d'éthanol à partir de diverses biomasses de première et deuxième génération ont été examinées. Au travers des publications de ces ACV respectives, une revue critique des forces et des faiblesses des différentes approches a été faite, afin de déterminer les conséquences de ces choix sur les résultats, y compris les limites du système, les procédures d'attribution et les catégories d'impact environnemental. Une étude de cas a été définie afin d'évaluer la performance de ces divers choix méthodologiques d'ACV. L'étude de cas permet la caractérisation des choix méthodologiques et la comparaison des diverses méthodes et leur conséquence sur les résultats. Ceci a mené à une méthodologie proposée pour la production d'éthanol selon l'étude de cas sélectionnée.

Les résultats de ce bloc montrent que pour l'étude de cas sélectionnée, lorsque l'éthanol est présumé être un carburant, le cycle complet de vie « du berceau à la porte» représente une frontière de système appropriée parce que l'utilisation et les phases de fin de vie sont similaires. Ceci donne également la possibilité de comparer la production d'éthanol à partir de différentes biomasses et d'identifier les points critiques du système de production. En termes de catégories d'impacts environnementaux, la sélection des catégories de mi-point est plus appropriée en raison d'une plus grande certitude à ce niveau. La méthode d'attribution peut avoir une forte influence sur les résultats. Dans le cas de production d'éthanol et d'électricité comme coproduit, il vaut mieux éviter l'allocation par extension du système afin de permettre l'inclusion de toutes les activités liées à la production d'éthanol et de l'électricité. Ces choix méthodologiques ont été ensuite utilisés dans d'autres scénarios de production d'éthanol afin de permettre une comparaison environnementale.

2. Sélection des paramètres d’évaluation environnementaux

Le second bloc avait pour objectif d’effectuer un examen systématique de mesures environnementales qui avaient été utilisées pour évaluer la production d'éthanol et de les interpréter afin d'arriver à un ensemble de mesures qui identifie les attributs environnementaux les plus importants du procédé de raffinage de l’éthanol. Dans ce bloc, divers scenarios de production d’éthanol ont été sélectionnés. Les schémas de procédé et les données de conception requis pour le scénario de base ont été définis afin de calculer les bilans de masse et les bilans énergétiques de tous les procédés. Le scénario de l’étude de cas a sélectionné la mise en valeur avant la mise en pâte (VPP) avec utilisation de l’hémicellulose pour produire de l’éthanol. La pâte, l’électricité et l’acide acétique font partie des coproduits de ce procédé. Les autres scénarios qui ont été définis incluent une nouvelle usine triticale paille-à-éthanol, une nouvelle usine de bois copeaux-à-éthanol lorsqu’intégrés dans une usine de pâte. Les scénarios d'éthanol sélectionnés sont illustrés dans la figure 2.

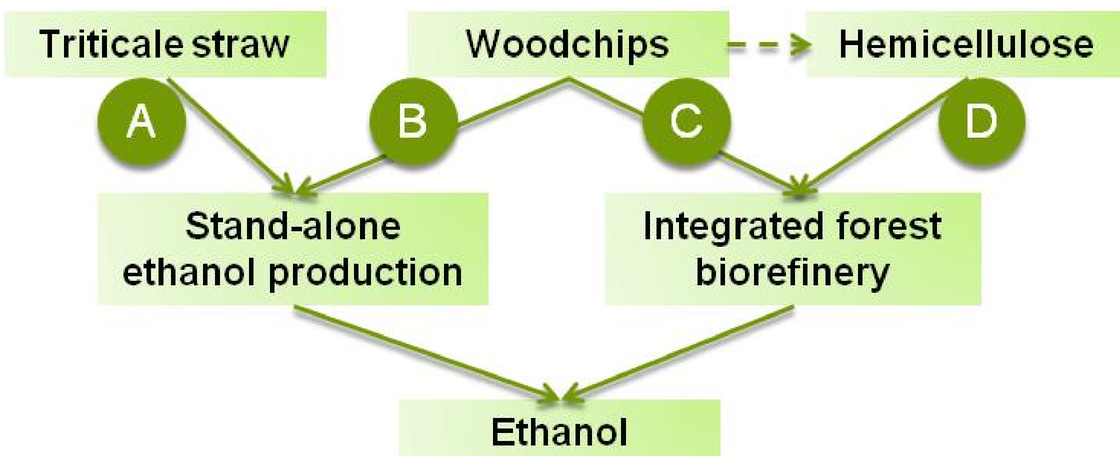

Figure 2. Différentes biomasses et diverses voies utilisées pour comparaison

Divers indicateurs ont été choisis, y compris des paramètres ACV et d’autres mesures environnementales, en se basant sur les modèles, la revue de littérature, les hypothèses et les données de conception de l’étude. Les paramètres ACV sélectionnés incluaient les produits inorganiques respiratoires, l’écotoxicité terrestre, l’occupation du sol, les catégories d’impact d’énergie non-renouvelable. L’utilisation des émissions de CO_2 et des indicateurs d'énergie a permis d'évaluer la réduction des émissions des gaz à effet de serre et la consommation d'énergie pour les divers scénarios de production d'éthanol. Cela a été également nécessaire vu que l'étape de prétraitement des diverses biomasses était différente selon les scénarios d'éthanol. Les produits inorganiques respiratoires et l'écotoxicité ont été retenus parce qu'ils étaient reliés à plusieurs étapes du cycle de vie de l'éthanol, y compris celles de la production de substrat, la pratique de culture et la route du processus en aval. L'occupation des sols était aussi importante puisque la culture de diverses biomasses pour la production de l'éthanol requiert différentes quantités de terres arables.

D'autres paramètres environnementaux ont été également sélectionnés car ils sont définis globalement et acceptés dans le monde entier. Les paramètres sélectionnés dans cette étude incluent entre autres l'intensité massique, l'efficacité énergétique et l'énergie allouée pour la production d'un MJ d'éthanol.

3. Interprétation des résultats

Le dernier bloc inclut l'interprétation des résultats, l'identification des paramètres clés et la comparaison des scénarios. L'identification des paramètres clés est le résultat des analyses de sensitivité et du scénario. À la fin de ce bloc soit à l'étape de l'interprétation de l'ACV, des opportunités d'amélioration de la performance environnementale de la production d'éthanol ont été identifiées pour tous les scénarios.

Les paramètres clés identifiés ont été les distances pour le transport (distance à la biomasse). Cette étude considère deux approches d'attribution : l'attribution physique (contenu énergétique des produits) et l'attribution économique (prix du marché des produits). La production d'électricité et de combustibles fossiles ont été aussi retenues comme paramètres clés pour l'analyse de scénario.

Résultats

Selon la méthodologie proposée pour faire des choix méthodologiques, la sélection des paramètres d'évaluation et des paramètres clés, les résultats de la caractérisation pour des paramètres ACV et d'autres paramètres sont résumés dans les tableaux 1 et 2.

Table1. Résultats ACV caractérisés pour tous les scénarios

Impact category	Unit	Triticale straw (Pathway A)	Woodchips (Pathway B)	Woodchips (Pathway C)	Hemicellulose (Pathway D)
Carcinogens	kg C2H3Cl eq	3.70E-03	3.33E-03	3.33E-03	4.67E-03
Non-carcinogens	kg C2H3Cl eq	1.16E-02	8.71E-03	8.73E-03	9.02E-03
Respiratory inorganics	kg PM2.5 eq	5.18E-04	4.82E-04	4.83E-04	5.81E-04
Ionizing radiation	Bq C-14 eq	1.10E+01	1.09E+01	1.09E+01	1.03E+01
Ozone layer depletion	kg CFC-11 eq	5.22E-08	4.96E-08	4.96E-08	4.81E-08
Respiratory organics	kg C2H4 eq	2.53E-04	2.48E-04	2.48E-04	2.70E-04
Aquatic ecotoxicity	kg TEG water	3.42E+01	3.05E+01	3.06E+01	4.31E+01
Terrestrial ecotoxicity	kg TEG soil	1.56E+01	8.94E+00	8.95E+00	9.49E+00
Terrestrial acid/nutri	kg SO2 eq	1.44E-02	1.29E-02	1.29E-02	1.47E-02
Land occupation	m2org.arable	8.95E-02	9.22E-02	9.22E-02	9.47E-02
Aquatic acidification	kg SO2 eq	3.10E-03	2.91E-03	2.92E-03	3.97E-03
Aquatic eutrophication	kg PO4 P-lim	3.47E-05	2.00E-05	2.00E-05	3.83E-05
Global warming	kg CO2 eq	5.07E-01	4.78E-01	4.79E-01	5.19E-01
Non-renewable energy	MJ primary	9.45E+00	9.09E+00	9.10E+00	9.02E+00
Mineral extraction	MJ surplus	8.47E-03	7.75E-03	7.75E-03	9.53E-03

Table2. Autres paramètres environnementaux pour tous les scénarios

Metrics	Triticale straw (Pathway A)	Woodchips (Pathway B)	Woodchips (Pathway C)	Hemicellulose (Pathway D)
Mass intensity (%)	23	32	39	45
Energy Efficiency (%)	41	58	53	53
MJ of fossil fuels/MJ of ETOH	7.0E-04	4.8E-04	1.5E-02	1.8E+00

Selon les résultats, tous les scénarios de production d'éthanol ont une meilleure performance environnementale lorsque comparés au procédé VPP (étude de cas). En ce qui concerne la catégorie d'impact d'écotoxicité terrestre, la production d'éthanol à partir de paille triticale est moins respectueuse de l'environnement que le processus VPP.

Des analyses de sensibilité montrent que l'approche d'attribution choisie influence davantage les résultats que tout autre paramètre analysé. La différence dans les résultats de l'impact environnemental varie jusqu'à 40 % entre les différentes approches d'attribution. C'est en raison de l'énergie nette des différents scénarios d'éthanol et du rendement de l'éthanol produit. Il convient de noter que l'utilisation de toute procédure d'attribution montre la même tendance dans les résultats, ce qui se révèle utile pour sélectionner le scénario le plus respectueux pour l'environnement.

L'analyse de scénario sur l'électricité contribue à améliorer la sélection du site de l'usine d'éthanol selon le réseau d'électricité qui est utilisé pour la production d'éthanol.

En termes de scénarios axés sur l'énergie, le changement de la source de combustible pour le procédé de génération de la vapeur n'affecte pas les résultats, sauf si des granules de bois sont utilisées.

Conclusion

Dans l'application de la méthodologie ACV pour tous les scénarios de production d'éthanol, l'analyse de sensitivité montre que l'approche d'attribution sélectionnée a une influence sur les résultats d'inventaire plus que tout autre paramètre ou choix méthodologique. La différence entre les résultats obtenus, en évitant l'attribution (par extension du système) et la répartition fondée sur les relations physiques et économiques, montre que les impacts environnementaux associés à la production d'éthanol par le biais de l'extension du système sont plus élevés. Les résultats finaux sont plus sensibles à 1) l'énergie nette de différents scénarios de production d'éthanol; 2) le rendement du procédé d'éthanol.

En outre, l'avantage supplémentaire de la méthodologie proposée est le choix systématique de paramètres ACV et autres mesures environnementales pour l'analyse environnementale de scénarios de production d'éthanol. Des indicateurs utilisés pour la comparaison des voies différentes d'éthanol peuvent fortement influencer le résultat de l'évaluation environnementale.

Par conséquent, l'ensemble des paramètres qui est en mesure de répondre correctement à la performance environnementale de production d'éthanol, quand on compare diverses voies, améliore la prise de décision.

Table of contents

List of tables

List of figures

List of abbreviations

ALCA	Attributional Life Cycle Assessment
CTBI	Canadian Triticale Biorefinery Initiative
CH4	Methane
CO	Carbon monoxide
CO	Carbon dioxide
CO2 Equivalent	Weighted sum of CO_2, CH4 and N_2O emissions using the weighting GWP factors defined below
CLCA	Consequential Life Cycle Assessment
DDGS	Distillers dried grains with solubles. Also sometimes abbreviated as DDG.
DOE	Department Of Energy
E10, E85 & E100	10%, 85% and 100% ethanol with balance gasoline by volume, respectively
g	Gram
gal	US gallon (3.785 L)
GHG	Greenhouse gases
GJ	Gigajoule (10^9 Joules)
GWP	Global warming potential over a 100 year period: CO2, 1; CH4, 21; N2O, 310
IFBR	Integrated Forest biorefinery
ISO	International Organization for Standardization
km	Kilometre
L or l	Litre
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
LCIA	Life Cycle Impact Assessment
lb	Pound (0.4536 kg)
mi	Mile (1.609 km)
MM	Million when applied to an imperial unit of energy
mpg	Mile per United States gallon
N2O	Nitrous oxide
NOx	Oxides of nitrogen
PM2.5	Particular matter
SO2	Sulphur dioxide
T	Tonne (1000 kg)
US	United States of America
USG	US gallons, (3.785 L)
VPP	Value Prior Pulping

List of appendices

Chapter 1- Introduction

1.1. Problem introduction and context

Ethanol as a renewable and biodegradable source of energy undoubtedly provides numerous environmental benefits. The most obvious is an increased reduction in carbon dioxide emissions which results in a reduction of the potential risks associated with climate change. Furthermore, many see ethanol as an opportunity to shift away from the reliance on non-renewable energy sources. Ethanol can be produced from biomass feedstocks containing sugar, starch and cellulose. Until now, sugar and starch-based feedstocks have been the primary raw materials for ethanol production, but competing food and feed demands and prices will eventually limit the expansion of this first generation of ethanol production. Since conversion of cellulosic biomass to ethanol potentially has many benefits, research should improve the environmental performance, as well as economic and social aspects in order to have a sustainable future for this second generation of ethanol production. Cellulosic biomass feedstocks are in general widespread and abundant, and do not cause food vs. feed conflicts. Furthermore, the potential for ethanol production from second generation of feedstocks in Canada is considered to be huge.

One of the new feedstocks for ethanol production in Canada are energy crops, in particular triticale. This is a man-made cereal crop developed by crossing wheat and rye. The Canadian Triticale Biorefinery Initiative (CTBI) is a 10-year R&D program developing triticale as a dedicated industrial biorefining crop for Canada. The CTBI network aims to develop new ways for using triticale as a feedstock for ethanol production and the manufacturing of biomaterials.

Another important feedstock in Canada is wood chips. Using this feedstock for ethanol production increases the potential of integrating ethanol production with a pulp and paper mill. The Canadian pulp and paper industry is a large biomass handler, and therefore they can be a host of cellulosic ethanol production. This means that Canada's pulp and paper industry has an important role to play in the development of a second-generation ethanol industry. Furthermore, this industry is aiming for continued environmental improvement.

In this context, process integration tools can be used to systematically evaluate new processes. The new biorefinery processes can be evaluated not only from a life cycle assessment, but also from a technical perspective. Life Cycle Assessment (LCA) is a product analysis technique that can be applied to different process alternatives in order to estimate the relative potential environmental impact the different alternative might have on the environment during their entire lifetimes. Another potential of application LCA in ethanol production includes the identification of improvement opportunities.

1.2. Holes in the body of knowledge

In the context of the ethanol biorefinery, there are many possibilities to determine the environmental performance. Different combinations of the allocation procedure, the system boundary of the study and the indicators used for the environmental evaluation result in different ethanol LCA outcomes. These differences occur because there is no one single methodology to make the correct methodological choices for an ethanol LCA assessment.

This hole in the body of knowledge is the driving force of this study in order to propose an appropriate LCA-based methodology for environmental evaluation of different ethanol biorefineries.

1.3. General objective

The title of this master is “Using Life Cycle Assessment (LCA) to evaluate the environmental characteristics of ethanol Biorefinery.”

The main hypothesis of this work is:

> *Different ethanol biorefinery processes manufacturing products and co-products are environmentally preferable under specific design conditions, which can be determined using a systematic LCA assessment process and appropriate performance metrics*

The sub-hypotheses divide the main hypothesis to three parts that are addressed in this work:

- The impact of LCA methodological choices such as different allocation approaches which describe environmental impacts for ethanol processes have different interpretations, whose results can be critically analyzed in order to identify environmentally-preferable biorefinery processes.

- Whereas many different LCA-based and other environmental evaluation metrics have been used to compare different ethanol biorefinery processes, it is possible to arrive at rational set of metrics whose interpretation permits a systematic environmental evaluation of a given biorefinery process.
- Based on the values calculated for the set of environmental metrics, it is possible to compare different ethanol production scenarios systematically.

The problem statement and hypotheses require that a methodology be developed in order to demonstrate the benefits of using LCA framework. This is addressed the following objectives:

- To assess the body of knowledge related to LCA studies for ethanol production using different feedstocks, in order to understand LCA-based approaches that have been used for allocating environmental burdens for evaluating ethanol biorefinery design alternatives.
- To identify a set of metrics that capture the most important environmental attributes of biorefinery processes in order to quantify the environmental impact of ethanol production.
- To apply an LCA methodology suitable for comparing the environmental impacts of ethanol production scenarios from different feedstocks by calculating and interpreting the selected set of environmental impacts using a case study basis.

Chapter 2- Literature review

2.1. Ethanol Biorefinery

2.1.1. Background of ethanol production

The use of ethanol as automobile fuel dates at the beginning of 1900 supported by Ford Company in United State. Ethanol was used to fuel cars into 1920s and 1930s when several efforts were made to sustain a U.S. ethanol program. However, after World War II, because of large quantity of petroleum fuels, there was little interest in ethanol production from agricultural crops [1].

Interest in ethanol was renewed in the 1970s. Its production jumped from 10 million gallons in 1970 to 175 million gallons in 1980. Since 1980, ethanol has enjoyed success. Its production in U.S. has increased about 12 percent per year, reaching 12 billion gallons in 2005. Figure2.1 shows the worldwide growth of ethanol from 1975 till 2010 [2].

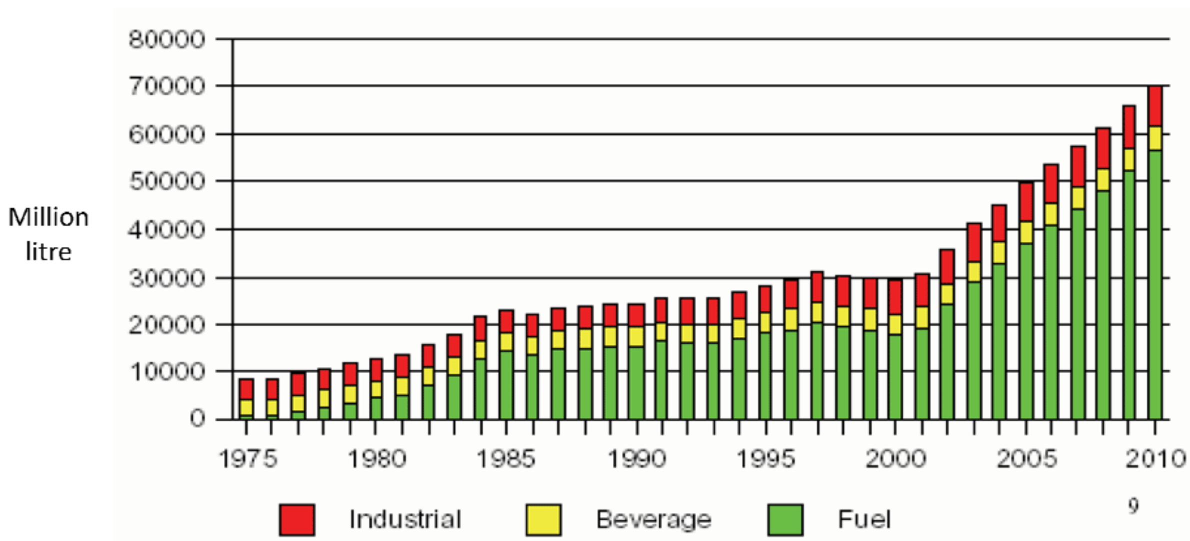

Figure2.1. Worldwide ethanol production by type [http://www.usfarmsinc.com/ethanol]

2.1.2. Main producers of ethanol

The major producers of ethanol are Brazil and United State which provide about 62% of the total ethanol production. The main feedstock in Brazil and US are respectively sugarcane and corn grain. Asia is the largest producer of ethanol from crops residues such as rice straw, wheat straw and corn stover. Its potential of ethanol production is up to 291 GL year $^{-1}$. The next highest region of ethanol production by 69.2 GL year^{-1} is Europe which provides their feedstocks mostly from wheat straw. In North America the main feedstock is corn stover which has the potential of ethanol production about 38.4 GL year $^{-1}$ [3]. Table2.1 illustrate the worldwide production of ethanol in year 2004 [4].

Table2.1.Worldwide production of ethanol [Kim et al., 2004]

Country	MG/Y	Country	MG/Y
Brazil	3989	Italy	40
U.S.	3535	Australia	33
China	964	Japan	31
India	462	Pakistan	26
France	219	Sweden	26
Russia	198	Philippines	26
South Africa	110	South Korea	22
U.K.	106	Guatemala	17
Saudi Arabia	79	Cuba	16
Spain	79	Ecuador	12
Thailand	74	Mexico	9
Germany	71	Nicaragua	8
Ukraine	66	Mauritius	6
Canada	61	Zimbabwe	6
Poland	53	Kenya	3
Indonesia	42	Swaziland	3
Argentina	42	Others	338
		Total	10770

2.1.3. Categories of feedstocks for ethanol production

Generally, feedstocks for ethanol production are divided into 3 main groups. These include sugar, starch and cellulosic biomass which are explained in the following sections.

2.1.3.1. Sugar-base feedstocks

Typically, microorganisms use the fermentable sugars mostly 6-carbon sugars such as Glucose as food and produce ethanol and other by-products. Therefore, biomass materials containing high levels of glucose or precursors to glucose are the easiest to convert into ethanol. Biomass materials containing high level of glucose sugar including sugar beet, sweet sorghum, and various fruits have high yield for ethanol production. But these materials are all in the human food chain and, except for some processing residues are generally too expensive to use for fuel ethanol production.

2.1.3.2. Starch-base feedstocks

The second group of feedstocks which can be used for ethanol production is starch-base feedstocks such as cereal grains (corn, rice, wheat, barley, oat ...), potato, sweet potato and cassava. These materials contain long chains of glucose molecules. By breaking these molecules to simple glucose molecules, ethanol can be produced by fermentation. The ethanol production process converts starch into ethanol. Therefore, the higher starch grains content, the higher ethanol yield is expected[5]. To break down the starch molecules to the simple fermentable sugars, one hydrolysis reaction is needed. Typically, hydrolysis is performed by mixing the starch with water to form slurry which is then stirred and heated to rupture the cell walls. Specific enzymes that will break the chemical bonds are added at various times during the heating cycle. Like sugar-base feedstocks, this group is also in human and animal food chain.

2.1.3.3. Cellulosic feedstocks

This group are in general very widespread and abundant. Being out of human food chain is an advantage of using these feedstocks and makes them to an inexpensive raw material. Besides, the use of cellulosic biomass in the production of ethanol has environmental benefits. Converting cellulose to ethanol increases the net energy balance of ethanol compared to converting corn to ethanol [6, 7].

Cellulosic materials consist of long chains of glucose molecules as do starch molecules, but have a different structural configuration. They contain lignin, hemicelluloses and cellulose and thus sometimes called lignocellulosic materials. Lignocellulosic biomass includes different sources such as agricultural residues, herbaceous crops, forestry wastes, waste papers and other fibrous wastes. These raw materials contain sugar, starch and lignocellulosic materials which have the ability to produce ethanol [8]. One of the primary functions of lignin is to provide support for the plant and thus, trees have higher lignin in comparison to grasses. Unfortunately lignin does not contain sugar and it is enclosed to the cellulose and hemicelluloses which containing sugars. In another word, cellulose and hemicelluloses are encapsulated by lignin and this makes more difficult to hydrolyze this group than the two other groups. Hemicellulose is also comprised of long chains of sugar molecules; but contains, in addition to glucose (a 6-

carbon or hexose sugar), contains pentoses (5-carbon sugars). To complicate matters, the exact sugar composition of hemicellulose can vary depending on the type of plant. Since 5-carbon sugars comprise a high percentage of the available sugars, the ability to recover and ferment them into ethanol is important for the efficiency and economics of the process. Recently, special microorganisms have been genetically engineered which can ferment 5-carbon sugars into ethanol with relatively high efficiency[9]. Development of cellulosic feedstocks is based on using non-grain, non-food-based feedstocks and the technology which cellulosic material into transportation fuel and other materials. These renewable sources play an important role in production of different materials in terms of reducing environmental impacts [10]. Because of the wide variety of biomass feedstock which can be used for energy production, we can separate them into specific groups such as agricultural waste, forest residue, municipal solid waste (MSW) and energy crops.

Agricultural waste available for ethanol conversion includes crop residues such as wheat straw, corn stover (leaves, stalks and cobs), rice straw and bagasse. Another group of cellulosic feedstocks is forest residues. This group includes underutilized woods and logging residues and wastes from forestry, arboriculture activities or from wood processing. Although forestry residues are not large in volume, they represent an opportunity to decrease the fire hazard associated with the dead wood presented in many forests.

Energy crops can be also mentioned as cellulosic biomasses. These are high-yield crops grown specifically for energy applications. This group includes fast-growing trees, shrub and grasses such as hybrid poplar, triticale, willow, switchgarss and alfalfa.

Another group of cellulosic feedstocks includes Municipal Solid Waste (MSW). According to DOE, MSW is defined as “residential, commercial and institutional postconsumer waste.” MSW contains a significant proportion of plant-derived organic material that constitutes a renewable energy source. Waste paper, cardboard, construction and demolition wood waste, and yard waste are examples of biomass resources in municipal waste.

2.1.4. Identification of potential feedstocks for ethanol production in Canada

The potential for ethanol from biomass in Canada is considered to be huge. It is estimated that if gathering and processing were economically feasible, there may be enough unused biomass from Canada’s forestry and farming operations alone in order to provide around 27% of the Canada’s current energy needs. The ethanol production industry in Canada is comprised mostly of small and medium-scale plants producing ethanol using agricultural crops as feedstocks. However, considerable advances in using lignocellulosic material extraction have been reported in the last decade [11].

One of the new sources for ethanol production in Canada is Triticale. Triticale which is a man made cereal crop developed by crossing wheat with rye is adapted widely in western Canada. It has higher grain yield even in unfavourable conditions, resistance to soil-climate conditions, tolerance to dryness, lower requirement of nutrient substances and fertilizer [12, 13]. Pejin et al. [2009] concluded that triticale has higher yield to ethanol in certain conditions compared to wheat and this conversion isn't effected by the absence of technical enzymes [12, 14]. It also required less temperature for preparation step[12]. As it is a local biomass in Canada, it could be a reasonable source for ethanol production.

Triticale is currently grown on an average of 200,000 acres each year in Canada. Compared to the country's major crops triticale has made a relatively small impact on industry. It should mention that one of triticale's main advantages for ethanol production is that the entire plant, including the seed and stalk, can be used. Indeed, triticale's low profile in the food-supply chain could make it an attractive feedstock option for ethanol production.

The Canadian Triticale Biorefinery Initiative (CTBI) is a 10-year R&D program developing triticale as a dedicated industrial biorefining crop for Canada. The CTBI network aims to develop new ways for using triticale as a feedstock for ethanol production and the manufacturing of biomaterials [15].

Another important source is woodchips. It is another opportunity for ethanol production as it is currently used in pulp and paper mills in Canada. This selection has the chance to produce ethanol stand-alone or with integration into pulp and paper mills. The pulp and paper industry is a large biomass handler with the know-how and personnel to operate a complex process industry, and therefore are a natural host of cellulosic ethanol production[16]. This means that Canada's pulp and paper industry has an important role to play in the development of an ethanol industry.

2.1.5. Stand-alone ethanol production

There are two primary conversion pathways of stand-alone ethanol production. These pathways include biochemical and thermochemical conversions which are explained separately in the following:

2.1.5.1. Biochemical pathway

The conceptual block flow diagram of biochemical ethanol production includes four different areas which shown in Figure2.2.

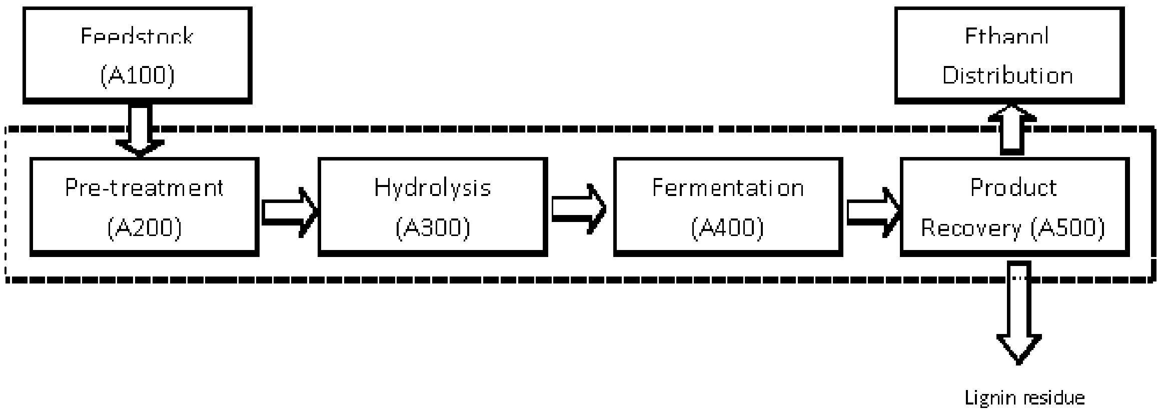

Figure2.2.Block flow diagram of biochemical pathway [Wooley et al, 199]

1. Feedstock area (A100): The process begins with feedstocks shipping to the feed handling area where they are washed, screened and reduced in size [1, 17].

2. Pre-treatment area (A200): In this step, the hemicelluloses fraction of feedstocks are broken down into a mixture of soluble five and six-carbon sugars by using dilute sulphuric acid catalyst at a high temperature for a short time. For neutralization, the washing step is used to remove acid from the solids. In some process configurations, hydrolyzate conditioning process (overliming) is needed to remove liberated by-products which are toxic for fermenting organism[1, 17].

3. Enzymatic hydrolysis or acid hydrolysis (A300): In this step which is also called saccharification, and sometimes joined with fermentation step, the pre-treated materials are saccharified with cellulase enzymes, releasing glucose. The detoxified hydrolyzate slurry is carried out in continuous hydrolysis tanks and anaerobic fermentation tanks in series. Cellulase enzyme is added to the hydrolyzate in the hydrolysis tanks that are maintained at a temperature to optimize the enzyme's activity. The inoculum, along with other nutrients, is added to the first ethanol fermenter along with the partially saccharified slurry at a reduced temperature. The cellulose will continue to be hydrolyzed, although at a slower rate, at the lower temperature. After several days of separate and combined saccharification and cofermentation, most of the cellulose and xylose will have been converted to ethanol.

Another configuration is a combined hydrolysis and fermentation (SSF – simultaneous saccharification and fermentation). There, the inhibiting sugars are fermented right after hydrolysis and therefore good hydrolysis yield is possible to achieve [1, 17].

4. **Product recovery (A500):** This step includes purification of ethanol from water and residual solids by distillation and molecular sieve adsorption. Solids from the distillation bottoms are separated and sent to the boiler to produce steam and electricity. The other possible product of fermentation is lactic acid. The separated water is also sent to wastewater treatment where they are treated and sent back to the process as recycled water [1, 17].

2.1.5.2. Thermo-chemical Pathway

This pathway converts biomass to fuel, chemicals and power. Thermochemical pathway divided into three technologies including gasification, pyrolysis and combustion. Currently, there are only two thermochemical ethanol production processes. The first one is the integration of thermochemical and biological system. In this process, biomass materials are gasified thermochemically and the bubbles of produced sygas are entered to fermenters under specific conditions to cause fermentation to ethanol production.

The second thermochemical ethanol production includes gasification of the biomass materials.

According to the development till now, gasification has the highest yield in near-term development among these technologies but pyrolysis can have an important role in future [1]. These technologies are explained in the following sections.

a. Gasification

In gasification a lignocellulosic feedstock is decomposed by thermal treatment in high temperature and controlled amount of oxygen conditions. The resulting gas mixture is called synthesis gas or syngas and is itself a fuel. The composition and quality of the gas are depend on a range of factors such as feedstock composition, feedstock water content, type of gasification reactor, temperature, pressure, gasification agents and presence or lack of catalysts. Gasification is a very efficient method for extracting energy from many different types of organic materials, and also has applications as a clean waste disposal technique.

The conceptual block diagram of thermochemical gasification is shown in Figure2. 3.

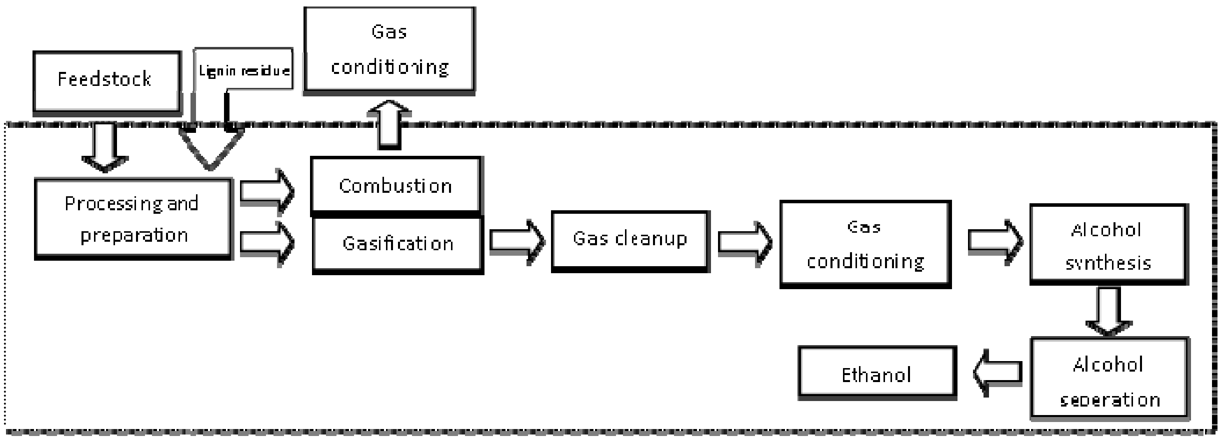

Figure2. 3. Block flow diagram of thermochemical pathway –Gasification [Wooley et al, 1999]

The gasification pathway for ethanol production has the following steps:

1. Feed processing and preparation: Maximum gasification system efficiencies are possible with dry and low-ash biomass. To achieve this goal, in this step biomass feedsocks are dried from the as-received moisture by using flue gases from the char combustor and tar reformer catalyst regeneration[1].

2. Gasification: In this step, heat for gasification reactions is supplied by circulating by hot olivine sand between gasifier and char combustor. Steam is injected into the gasifier in order to stabilize the flow of biomass. The biomass is converted to syngas component (CO, H_2, CO_2, CH_4 ...), tars and solid "chars". At the exit of the gasifier char and sand are separated from the syngas by cyclones. Air consisting controlled amount of oxygen is injected into the bottom of the gasifier as a carrier gas for the fluidized bed. It is also used as an oxidant for burning the char and coke. The hot sand with the temperature over 1800 ^{o}F and residual ash from the char is carried out of the combustor and separated from hot gases by another pair of cyclone. The first cyclone is set to capture mostly sand and the second one is designed to detain the ash and any sand which passing through the first cyclone. The separated hot sand from the first cyclone is send back into the gasifier to provide the required heat for the gasification reactions. The effluent of the second cyclone is cooled and moistened to minimize dust and sent for disposal [1, 18].

3. Gas cleanup: This step contains the removal of contaminants from biomass gasification products gas. Gas cleanup is multi-step approach which varies according to the projected end use of the product gas. But normally, this step consists of following operations such as reforming tars and acid gas in an isothermal fluidized bed reactor. In this step, de-activated reforming catalyst is separated from the effluent syngas and regenerated on-line. Then the hot syngas is cooled by heat exchanging with the steam cycle and additional cooling is carried by water scrubbing. In this scrubber impurities such as particulates and ammonia are also removed from residual tars. The excess scrubber water is sent to waste water treatment section and the cooled syngas is entered to the gas conditioning section[1, 18].

4. Gas conditioning: The main purpose of this unit is to adjust the amount of hydrogen sulphide and final hydrogen carbon monoxide ratio to an acceptable level for the alcohol synthesis step[1, 18].

5. Alcohol synthesis: The cleaned and conditioned syngas is converted to mixed alcohols or Fischer-Tropsch hydrocarbons in this step. The mixture is cooled through heat exchange with the steam cycle. Then by condensing, the liquid alcohol and unconverted syngas are separated in order to recycle back the unconverted syngas into the entrance of the unit[1, 18].

6. Alcohol separation: The alcohol stream from the previous step is first depressurized and then dehydrated using vapour-phase molecular sieves. The hydrated alcohol stream is then injected to the main separation column in order to split methanol and ethanol from the higher molecular weight alcohols. The overheads are carried to the second column to separate the methanol which is then used to flush the absorbed water from the molecular sieves. This mixture including methanol and water is recycled back to the entrance of alcohol synthesis reactor to increase the yield of ethanol and higher alcohols[1, 18].

Ethanol yield from syngas in thermochemical process is up to 50% .But in some processes that first methanol is produced and then used catalysts to produce ethanol; yield can be increase in about 80%.

b. Pyrolysis

Pyrolysis is a process that uses heat to decompose biomass in the absence of oxygen. Ground up biomass is exposed to temperatures of just under 500°C, converting it to char and gases. The gases are then rapidly cooled, and some of them condense into pyrolysis oil.

The pyrolysis oil is a mixture of water and many different organic compounds. It can be burned as is for fuel, or can be refined to yield useful industrial chemicals and higher quality fuel. The gases that are produced during pyrolysis can be burned to create heat to keep the process going. The thermochemical pyrolysis process has four main steps which are shown in Figure2.4.

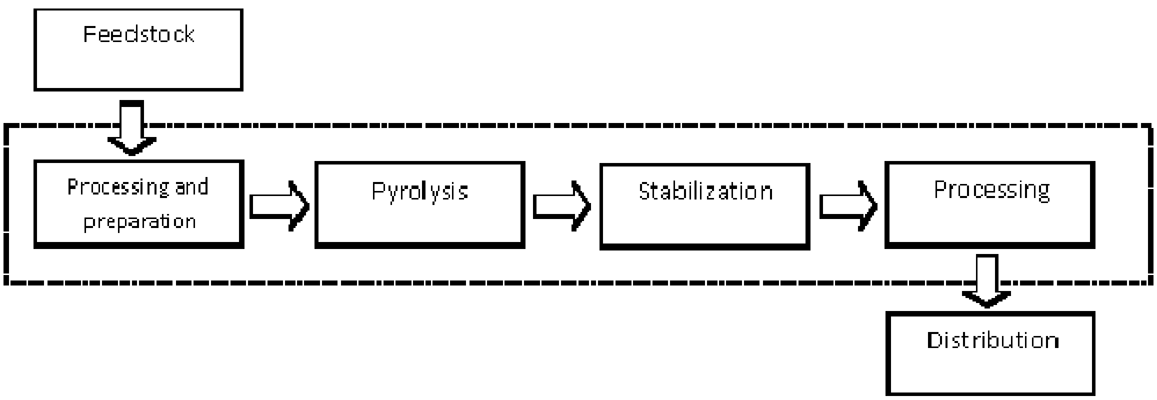

Figure2.4. Block flow diagram of thermochemical pathway-Pyrolysis [Wooley et al, 1999]

1. Feed processing and preparation: Such as gasification, pyrolysis system efficiencies are depended on biomass properties such as moisture content, composition, impurity concentrations and ash content. Maximum pyrolysis system efficiencies are possible with dry and low-ash biomass. To achieve this goal, in this step biomass feedsocks are dried from the as-received moisture by using flue gases from the char combustor and tar reformer catalyst regeneration[1].

2. Pyrolysis: This step is the thermal decomposition of biomass in the absence of oxygen. The reactions occurred in pyrolysis need lower temperature than gasification and produce primary liquid products instead of gas. These primary materials can be converted to other products which their characteristics depend on the processing conditions [1].

3. Cleanup and stabilization: This step consists of removing water, ash and particulates by filtration or any other similar processes. Cleanup and stabilization convert bio-oil into a product suitable for feeding to a petroleum refinery.

4. Processing: After cleanup process, we need a step to provide biofuel alternatives to ethanol.

2.2. Integrated ethanol production

One of the emerging concepts in the ethanol process is the idea of the integrated forest biorefinery. It is necessary to study the retrofitting of existing facilities by integrating them with the concept of Biorefinery such as ethanol production and give the opportunity to add the new production lines. Process integration provides an attractive framework for retrofitting existing facilities or integrating new facilities with neighbouring plants. In particular this work helps to reduce energy and material utilities and to enhance the advantages of the original facility and the ethanol biorefinery. Integration may take several forms including [19]:

- Equipment sharing
- Feedstock allocation and/or substitution
- Energy integration
- Mass integration
- Waste handling

These advantages gives the need to develop a systematic and generally applicable design procedure which guides process engineers as they make their decisions in retrofitting and integration.

The Canadian pulp and paper industry currently faces many challenges. The significant environmental issues and the increasing price of energy are making it increasingly difficult for Canadian pulp and paper companies to survive the global market place. This requires the companies to propose the integrated forest biorefinery into their existing industries [20, 21].

2.2.1. Conventional Kraft pulp mill

The Kraft process has been established as the most economical chemical pulping process during 50 last years. In the current processes about 20 and 30% of wood weight is dissolved in the waste pulping liquor in the form of hemicellulose and lignin respectively. The liquor consisting of these dissolved materials is combusted to produce steam and electricity[22].

2.2.1.1. Process description

The Kraft pulping process involves the digesting of wood chips at elevated temperature and pressure in white liquor which is a water solution of sodium solfite and sodium hydroxide. The white liquor chemically dissolved the lignin that binds the cellulose fibers together. Generally, in Kraft pulping there are two types of digester systems, batch and continues. Most of installations in Kraft pulping are batch digesters. In this type of digesters, after cooking, the contents are sent to a tank and pulp washers respectively. After these steps the cooking liquor is separated from pulp. The pulp then is processed through various stages of bleaching and finally it is dried to have the final product. The spent cooking liquor and the pulp wash water are collected as black liquor. The black liquor is concentrated and burned in a recovery boiler in order to generate the heat process and convert sodium sulfate to sodium sulphide. Inorganic chemical at the bottom of boiler is collected as a smelt and dissolved in water to form the green liquor. This liquor is then transferred to a causticizing tank where quicklime is added to convert the solution to white liquor for returning to the digester system[23].

Figure2.5 shows a typical Kraft pulping and recovery system[23].

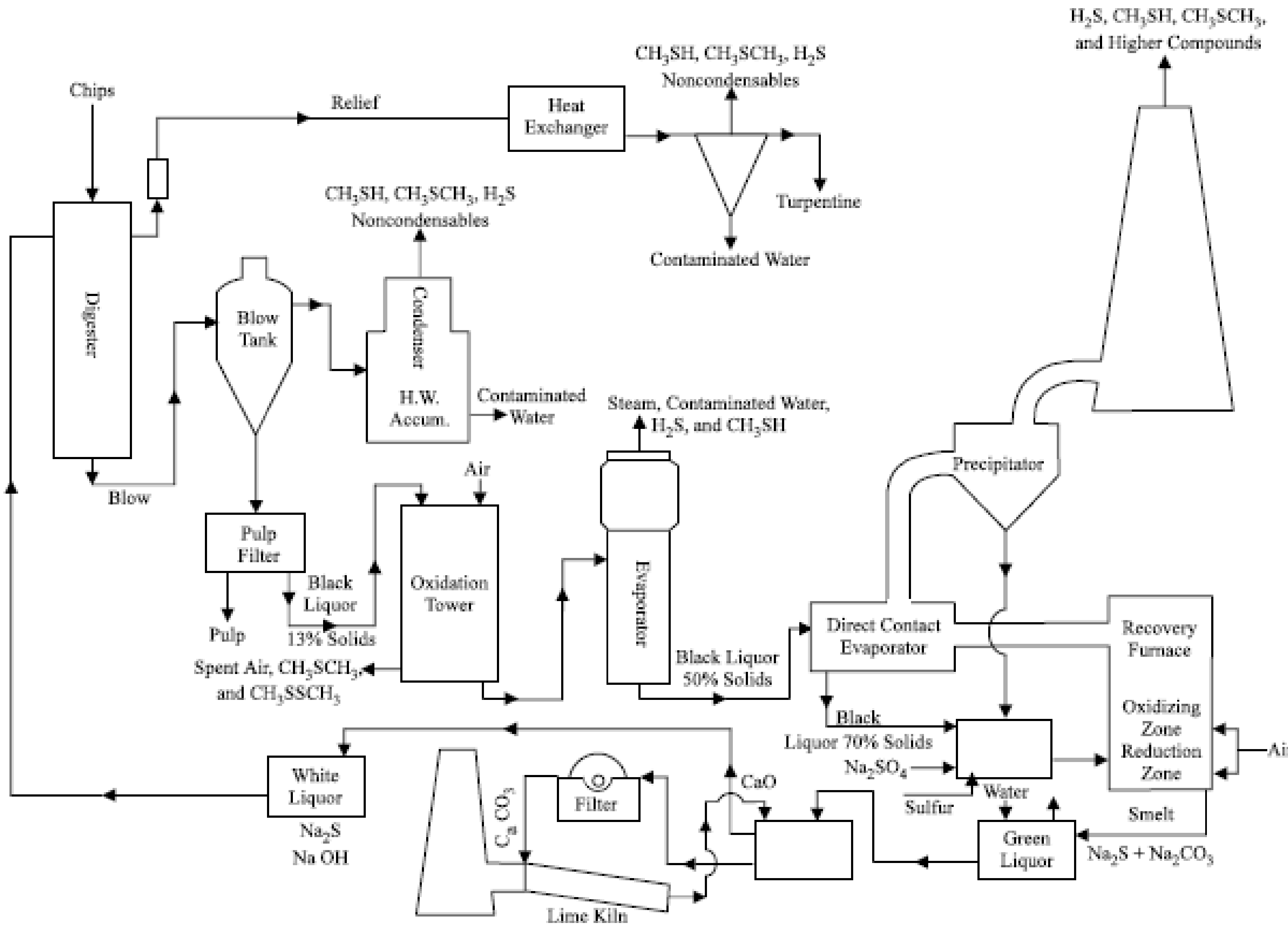

Figure2.5.Typical Kraft pulping [EPA]

For process heating, Kraft mills need steam which is provided in-site. This steam is provided in recovery and hog fuel boilers. The energy needed for driving equipments such as lime burning is supplied by burning coal, oil, natural gas, bark and wood[23].

There are some key bottlenecks in the Kraft pulping process which are important to be assessed. These are including:

a. Pulp digester: Digesters are very capital intensive and their performance is of paramount importance to maximize the produced pulp quality and yield, reduce the overall operating costs and minimize the adverse environmental impacts of pulp mills. With more pulp and paper companies replacing their pulping processes with modern fiber lines using continuous digesters to meet increasing competitiveness in the global market and tighter environmental regulations, there is an increasing need for improved control of continuous digesters. One of the key technical challenges to operation of this unit is the management of production rate changes and grade swings between hardwood and softwood feedstocks.
b. Recovery boiler: The recovery of energy and chemicals from pulping process waste liquors is an important step in Kraft pulping and the total pulp production capacity is heavily dependent on the capacity and availability of the recovery boiler. When the capacity of the boiler (The amount of black liquor to be treated) has to be increased, the bottleneck in a recovery boiler is usually the boiler section. The scale of production is important. Most of the mills increase their pulp production until the recovery boiler becomes the bottleneck restricting any further increase in production.
c. Reusing of condensates from black liquor evaporation in the plant: Odour is a critical parameter in some paper products. Bad odours in process water can be transferred to pulp and paper. Consequently, the removal of malo-dorous substances from black liquor condensates may be needed before reuse. The effect on bleaching characteristics and on the smell and taste of pulp and the condensate composition and chemical consumption used for the bleaching should be carefully analyzed.
d. Lime Kiln: Since the lime kiln is often the bottleneck to higher pulp production rates, contaminants in the re-burned lime can decrease overall pulp production and concomitantly increase energy costs.

2.2.2. Different concepts of integrated ethanol biorefinery

The integration of ethanol Biorefinery into an existing pulp and paper mill has different concepts including short and long term.

Some of the current pulp and paper mills are already working as elementary forest Biorefinery which is a short-term concept. As it is shown in Figure2.6, the energy produced in the system is exchanged among different parts of the process to avoid the production of energy separately. In the optimized future forest Biorefinery or longer-termer concept, it is expected that the biorefinery will expand more in order to produced not only energy but also bio-based chemical. The principals of this two concepts are shown in Figure2.7 [24].

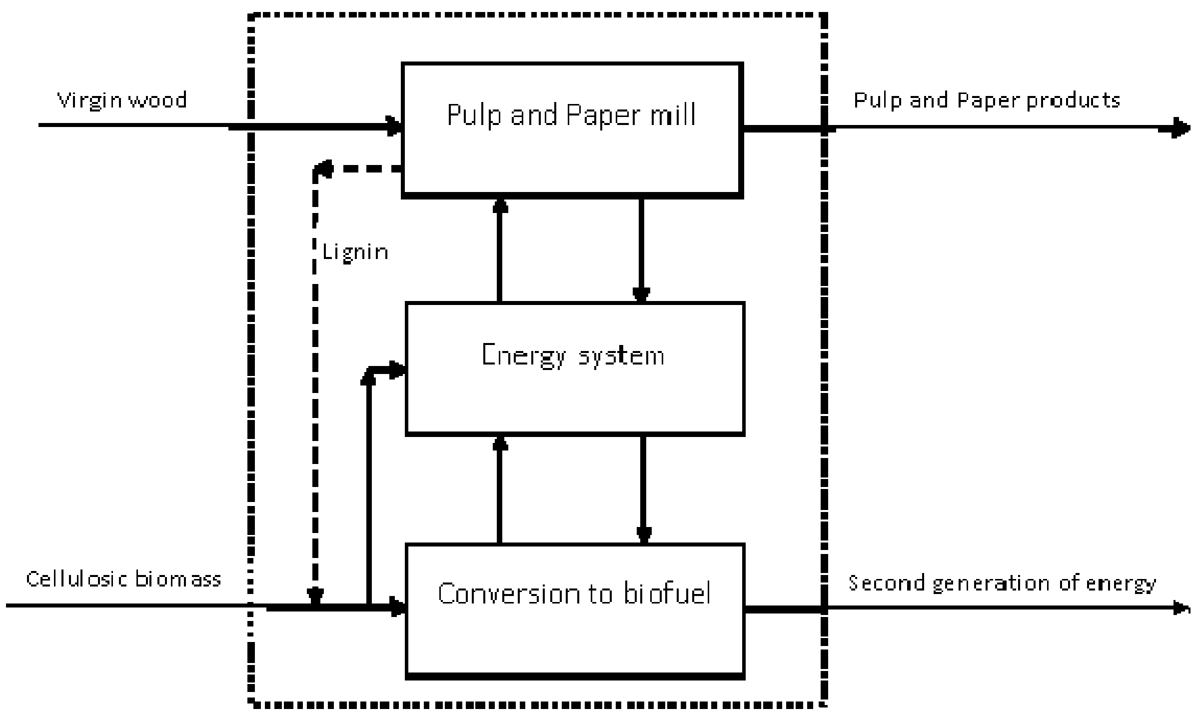

Figure2.6. Short-term concept of integrated ethanol biorefinery

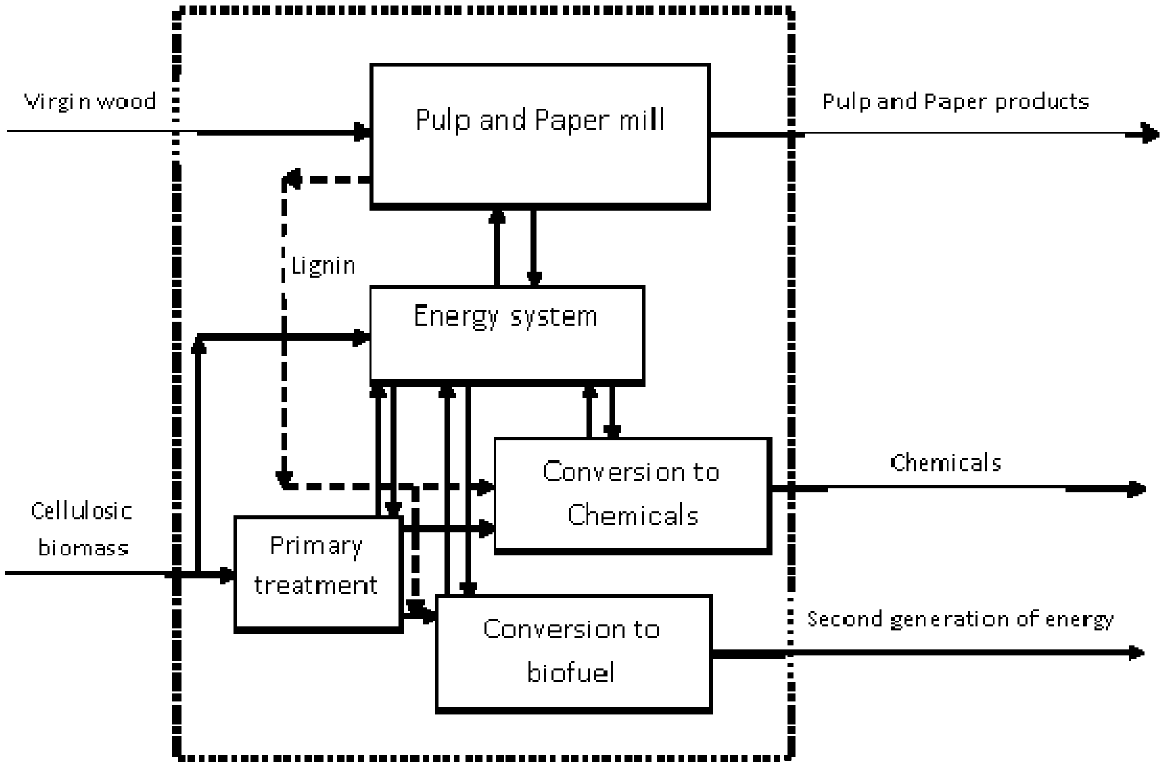

Figure2.7. Long-term concept of integrated ethanol biorefinery

There are always some challenges associated with the integration of ethanol biorefinery with an existing pulp and paper mill which affect the performance of integration. These challenges include:

1. Design feedstock and feedstock flexibility
2. Overall plant efficiency targets and the trade-off with capital cost
3. Waste water discharge guidelines (affects auxiliary load)
4. Emission limits or standards
5. High temperature heat recovery integration
6. Low temperature heat recovery integration
7. Steam generation conditions
8. Utility balance
9. Brownfield site and use of existing equipment
10. Co-production or poly-generation including steam, and other products

2.2.2.1. Parallel ethanol production with pulp mill

This concept includes a novel use of two processes, the first of which provides ethanol (main product) and energy (co-product) in the form of steam. This steam is then sent to the pulp mill in order to provide the additional energy required for the pulping. The careful management of the extent to which the fuel resource is used in a pulp mill actually reduce the purchased energy provided by fossil fuels. The concept of ethanol production is the same as the stand-alone woodchips-to-ethanol through biochemical pathway[17]. Pulping process includes receiving, debarking and chipping the logs. The pulp process is also Kraft pulping mill which is explained previously [23, 25, 26].

2.2.2.2. Value Prior Pulping (VPP)

Value Prior Pulping (VPP) which is a longer-term concept of ethanol Biorefinery includes the “near-neutral” hemicellulose pre-extraction integrated into an existing hardwood Kraft mill. This process starts with wood extraction for hemicellulose removal, flashing of the extract to produce steam, recycling a portion of extract back to the extraction vessel in order to raise the solids content of the extract, sulphuric acid hydrolysis for conversion of carbohydrates into mono sugars, filtration to remove lignin, liquid-liquid extraction, distillation to remove acetic acid and furfural followed by liming step, fermentation of sugars for ethanol production and finally distillation of product[25]. It is assumed that the existing Kraft pulp mill is facilitated to produce the market pulp as well as ethanol and acetic acid using the hemicellulose extraction process. When we integrate the VPP process into this existing pulp mill, the amount of process heating steam needed is increased. This raise is covered by extra purchased biomass in the mill after modification in Hog fuel boiler. But, the amount of purchased fossil fuels for burning lime is decreased in a VPP process. Usually, efficiency for conversion of biomass to electricity in existing biomass based power systems ranges from 10% to about 28%. In this study this amount is 20%.

2.3. Overview of Life Cycle Assessment (LCA) methodology

2.3.1. General methodology

Based on net energy analysis studies, which were first published in 1970s, there has been a substantial development of life cycle methodologies to assess the energetic and environmental impacts of product systems from cradle-to-grave, named Life Cycle Assessment (LCA). Life cycle assessment is a technique for assessing the environmental aspects associated with a product over its life cycle. LCA provides the more quantitative and scientific basis for all new concepts. In many cases LCA feeds the internal and external discussions and communications. Being active in LCA means to be able to communicate the environmental impacts of products and business processes[27]. An LCA study offers a comprehensive picture of the flows of the materials and energy through a system and gives the objective basis for comparison. LCA is based on system analysis, treating the product process chain as a result of input and output exchanged sub-systems.

According to ISO 14040 four standards are designed for LCA [28]. These standards include:

1. Goal and Scope definition
2. Inventory analysis
3. Life Cycle Impact assessment
4. Interpretation

Figure2.8 shows the relationship between these four phases and general LCA application[28].

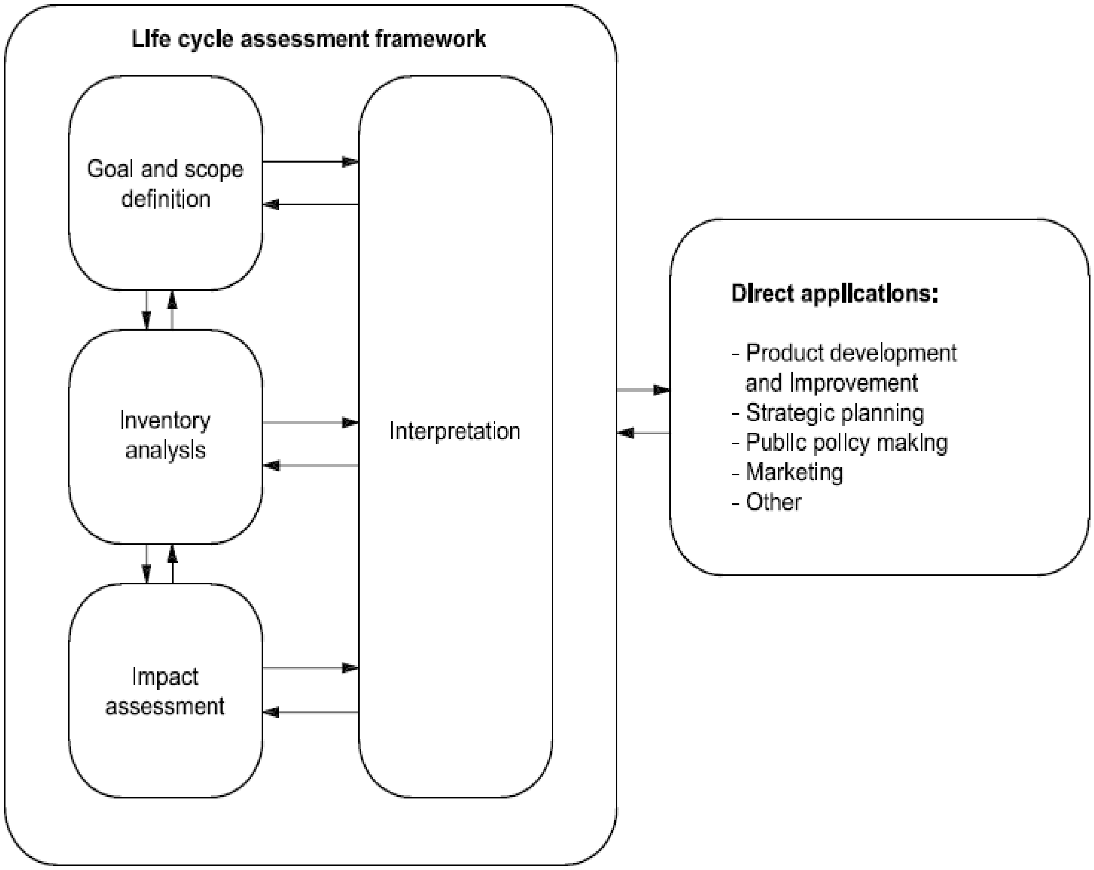

Figure2.8. Stages of an LCA [ISO 14040, 2006]

2.3.1.1. Goal and scope

Identification of goal in LCA studies is a crucial phase. According to the goal, we can recognize the scope and thus the requirements on the modelling. Different scope and purpose gives different methodologies so knowing the specific goal helps analyzer to set the appropriate methodology. Goal identification in LCA studies is recognized according to the context of the study such as why this study is done, how and by whom the results are going to be used. It is necessary to transform a general goal into specific ones in order to make appropriate methodological choices in the subsequent modelling [27]. There are some methodological choices in each LCA study which have to be identified appropriately based on the goal and scope of the study. These methodological choices are explained in the following sections.

a. **Functional unit:** The functional unit is the unit which the results of study are related to but it is not always associated with the production or consumption volumes. It is related to product function. Identifying functional unit is complicated because the comparative products are rarely in the same units. They may not be in the equal quantity or one of the products has additional functions. The functional unit must represent the function of the compared options in a reasonably way. At the same time, the compared options may complete the function more or less, or have qualities in addition to the one described by the functional unit. One way dealing with these kinds of problems is defining a minimum level that all the options must fulfil [27].

b. System boundaries: It consists of the activities included and/or excluded in the study. The system boundaries should be set in order to include all important burdens in the system such as energy production used for converting biomass to ethanol, and avoid all the insignificant streams, the latter for simplicity of the model and it should be performed carefully [27].

c. Allocation procedure: Sometimes, several products share the same process (es). In this case, identification of the environmental load for each product is difficult and this is named as allocation problem. Generally, there are three basic cases when allocation problems are encountered. These are included multi-output, multi-input and recycling as shown in the following Figure2.9.

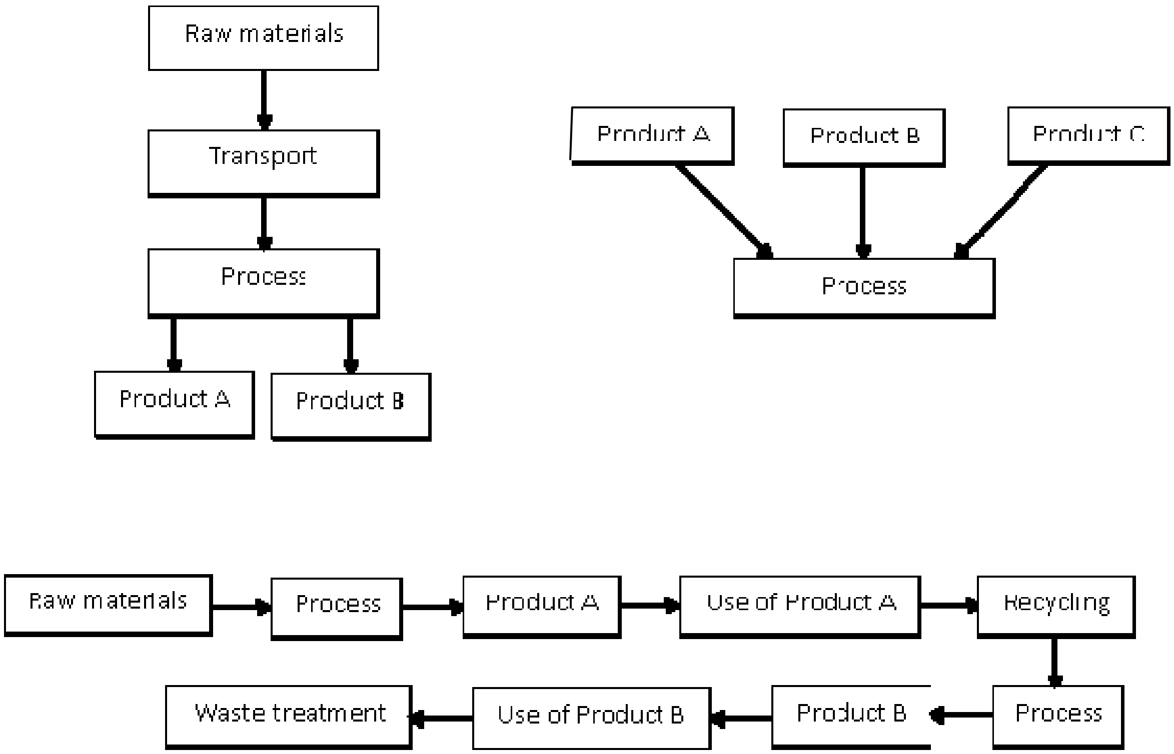

Figure2.9. Different multi-functional processes

ISO standard recommends an order of preference between allocation methods. This allocation procedure is as follows[29]:

- The allocation should be avoided by dividing the unit process into two or more sub-processes or expanding the product system to include the additional functions related to co-products.
- Where allocation cannot be avoided, the partitioning model should be applied. This partitioning should reflect not only mass or molar flow of by-products but also the physical relationships.
- Where physical relationship cannot be used alone, allocation should be based on the other relationship such as economic value of the products.

The choice of allocation approach influences the final results more considerably than other parameters investigated. As a result, the allocation procedure is a critical part of determining environmental burdens. According to the ISO 14041, whenever several alternative allocation procedures seem applicable, a sensitivity analysis should be conducted. Besides, a sensitivity analysis to allocation rules is useful in reduction of uncertainty choices in LCA[30].

It is also concluded that selection of allocation procedure is performed based on the type of LCA [31]. Generally, two different LCA approaches, attributional LCA (ALCA) and consequential LCA (CLCA), were identified and described [32-34]. ALCA describes the pollution and resource flows within a chosen system attributed to the delivery of a specified amount of the functional unit. CLCA estimates how pollution and resource flows within a system change in response to a change in output of the functional unit[35]. The distinction between ALCA and CLCA was developed in the process of resolving the methodological debates over allocation problems and the choice of data. Within ALCA, avoiding allocation by using system expansion to handle co-products is optional, while co-product allocation is most frequently used. Avoiding allocation by system expansion, however, is the only way to deal with co-products within CLCA, as it reflects the consequences of a change in production[36].

2.3.1.2. Life Cycle Inventory Analysis (LCI)

Inventory analysis means to make a flow model of technical system. Activities in this section include[27]:

- Making a detailed flowchart according to the goal and scope definition.
- Collecting data for all activities in the system by documentation of collecting data.
- Calculating of the environmental impacts of the system according to the functional unit.

As mentioned in goal and scope section, a general flowchart is needed. But in this level of study, the flowchart is developed in much more detailed. It has to include all modelled activities and the flows between them[27].

2.3.1.3. Life Cycle Impact Assessment (LCIA)

LCIA is the description of environmental impacts in an LCA study. LCIA is also useful for making results more comparable. LCIA has following steps such as [27]:

- **Impact category definition:** To set the impact category depends on the definition and categories which have been identified in the goal and scope.
- **Classification:** When the results of LCI study are sorted and assigned to the various impact categories, it will be classification. According to this step we recognise which type of pollutant and resource use is leaded in the study.

- **Characterisation:** The calculation of environmental impacts per category is named as characterisation. In the other word, this is a quantitative step. Here the sizes of environmental impacts are calculated per category by using category indicators.
- **Normalisation:** By relating the characterisation value to a reference value, the normalisation will be defined. This aim a better understanding of the environmental impacts caused by the system. Normalisation is meaningful when the comparison is made between the total impact of the total use of the product and the total impact in the region. While the selection of the methodological choices will affect the results because of fundamental differences in modeling, the choice of a normalization reference aims at better interpreting the results, which is critical if LCA is to be used for practical decision-making. Normalization should be applied in order to determine which environmental impact is more significant in the study. The normalization approach should fulfill the horizon of the study. Norris [37]discussed the internal and the external approaches for normalization in LCIA. In internal approaches, the score of a particular category is divided by a function of the values obtained for the studied alternatives for that category. External approaches are generally linked with the contextual view in which the relative significance of results in different impact categories is assessed. External normalization allows the evaluation of the relative significance of a category's result to the global impact of a chosen referential system. This system should be justified based on the geographical location and the technical characteristics of installation.
- **Grouping:** It includes sorting the characterisation results into one or more groups. It helps to analyze and present the results in a better way.
- **Weighting:** It is defined as the quantitative and qualitative procedure where the relative importance of an environmental impact is weighted against all the others. It will be accessible by the weighting factors for each environmental impact.
- **Data quality analysis:** This category defines the uncertainty and sensitivity of LCIA results. For example, studying about the most polluting activities in LCA, the most crucial inventory or impact assessment data, the importance of different methodological choices and degree of uncertainty of the results can be categorized in this step.

Among the mentioned steps, characterisation is the central method for LCIA study. It is based on scientific methods for describing different environmental impacts. Characterisation methods of pollutant are a combination of physico-chemical properties and the fate of pollutant in the environment. Because of the complexity of the environmental systems, various characterization methods based on different modelling principals are defined. These impacts categories include resources, land use, global warming, ozone depletion, toxicity, photo-oxidant formation, acidification and eutrophication[27].

2.3.1.4. Interpretation

The process of assessing results in order to draw conclusions is called interpretation. The use of different diagrams is helpful in this process. Evaluations of the strength of conclusion drained in an LCA study are also part of the interpretation phase. Such evaluations involve sensitivity and uncertainty analyses and data quality assessments[27].

The term life cycle interpretation is defined in the ISO 14040 standards as the "phase of Life Cycle assessment in which the findings of either the inventory analysis or the impact assessment, or both, are combined consistent with the defined goal and scope in order to reach conclusions and recommendations." [28]

2.3.2. Critical review of LCA ethanol production

2.3.2.1. Characterization of LCA studies

The results of 26 LCA publications were characterized in order to have a critical review of ethanol environmental performance. The main conclusions of these articles are summarized in Table2.2 . The complete information for the reviewed article is available in Table D.1 in the Appendix D. These LCAs cover various regions and feedstocks and evaluation of different environmental impacts for ethanol production. These studies published between 2001 and 2008 were reviewed to develop an overall picture of LCA methodological evaluation for ethanol production. One of the important criteria for the selection of these publications was the LCA methodology used in these assessments was described and several environmental impact categories were used. They were also selected based on their allocation procedures associated with various co-products in ethanol production.

These reviewed LCAs reported in this study include two kinds of feedstocks for ethanol production:

- First generation: including corn grain, cassava, sugar beet, wheat grain and sugarcane
- Second generation: including agricultural and forest residues, wood and municipal solid waste

Table2.2. The summary of reviewed articles

References	Main conclusion
Panray Beeharry [2001]	Sugarcane bioenergy systems stand out as promising energy projects for environment.
Kadam [2002]	Converting of bagasse to ethanol generally has less environmental impacts in compare to burring it.
Kim et al. [2002]	Sensitivity analyses show that the choice of allocation procedures has the greatest impact on fuel ethanol net energy.
Fu et al. [2003]	The reduction of GHGs by using biofuel is particularly sensitive to the source of energy used to produce the process steam.
Durante et al.[2004]	Ethanol reduces greenhouse gas emissions compared to conventional gasoline.
Sheehan et al. [2004]	The answer to the question of whether stover is a sustainable source of energy for transportation is highly depended on the chosen methodology.
Kemppainen et al. [2005]	The environmental impacts of ethanol are highly depends on the type of feedstocks.
Kim et al. [2005]	The energy consumed in ethanol production is smaller than the energy content of ethanol.
Hu et al.[2006]	Environmental emissions of the cassava-based ethanol are changeable based on the design variables.
Malca et al.[2006]	The optimum use of co-products in ethanol production is needed to improve the energy efficiency.
Kim et al. [2006]	Using ethanol in the form of E_{10} and E_{85} has different performance based on the chosen environmental impacts.
Bernesson et al.[2006]	The results were dependent on the allocation method used between the ethanol fuel and co-product.
Botha et al. [2006]	Using fuel ethanol has better results in term of environmental impacts.
Baral et al.[2006]	Ethanol has lower returns on energy investment (rE) in comparison to gasoline.
Fleming et al.[2006]	The biofuel options hold the potential for significant reductions in non-renewable energy use and GHG emissions compared to gasoline/diesel fuel.
Hill et al.[2006]	Energy conservation of non-food biofuel has better environmental benefits over the longer term.
Reijnders et al.[2007]	Presently, there is a trades-off between lignocellulosic crops and starch or sugar derived ethanol regarding life cycle fossil fuel inputs or greenhouse gas emissions.
Beer et al.[2007]	Using of ethanol has demonstrable greenhouse gas benefits in both light and heavy vehicles.
Weiss et al.[2007]	The results of this study demonstrate that the potential of bio-based products to reduce negative environmental impacts compared to their fossil counterparts strongly depends on the assumptions used in the methodology.
wismer et al. [2007]	Bio-ethanol as a gasoline/ethanol blend is an important means to reduce greenhouse gas emissions.
Curran [2007]	The results of the LCA study are highly depended on the allocation methodology which is based on the case study and assumptions.

Kalogo et al. [2007]	Producing ethanol from MSW can contribute to reducing dependence on non-renewable petroleum resources and reducing GHG emissions.
Gabrielle et al. [2008]	The factors of calculation the environmental impacts should be addressed based on local characteristics rather than on national or global averages.
Nguyen et al. [2008]	Ethanol used in form of E_{10} or E_{85} helps the reduction of energy use and GHG emissions but its conversion step is the main source of energy use and most environmental impacts.
Kim et al. [2008]	Using ethanol E_{10} derived from corn would reduce non-renewable energy and greenhouse gas emissions but would increase acidification, eutrophication and photochemical smog, compared to using gasoline as liquid fuel.
Leng et al.[2008]	Use of different allocation approaches can have significant impacts on calculated biomass ethanol fuel-cycle energy use and energy efficiency.

As it is shown in the table, the results of these studies are various considering different methodological choices such as system boundaries, allocation procedures and environmental impact categories. These inconsistencies in ethanol LCAs arise because there is not one single methodology for selecting these choices which are key issues and have to be identified and adapted in ethanol LCA. We did not correct the differences but we compared the obtained results and the consequences of these different choices in each respective LCA publication in the following sections.

a. System Boundaries

As mentioned before, one of the methodological choices in each LCA is selecting the appropriate system boundary. Ideally, an LCA consists of all four stages including raw materials acquisition, manufacturing, use and waste management. Some studies have used a cradle to grave approach [38-50] and others have used the cradle to gate approach [51-57]. It is also suggested another approach which is the allocation of boundaries between the system analysis, the foreground system, and the background system (Indirect effects). This approach have been used rarely in the reviewed LCAs for ethanol production[55].

The critical review shows that the “cradle-to-grave” boundary in ethanol production leads to a holistic perspective of environmental impacts but the choice of the “cradle-to-gate” seems more appropriate. It enables the results and fuel energy efficiencies to be analyzed in a variety of different ways [57].

b. Environmental impacts

Based on the literature review, it is resulted that various LCAs used different environmental impact categories for their evaluation which affect the results [40, 50, 57, 58].

Figure2.10 shows the breakdown of LCA studies by the field of mostly used environmental impact categories for ethanol production. Generally global warming, acidification, eutrophication and energy use are the most selected categories which are considered in ethanol LCAs.

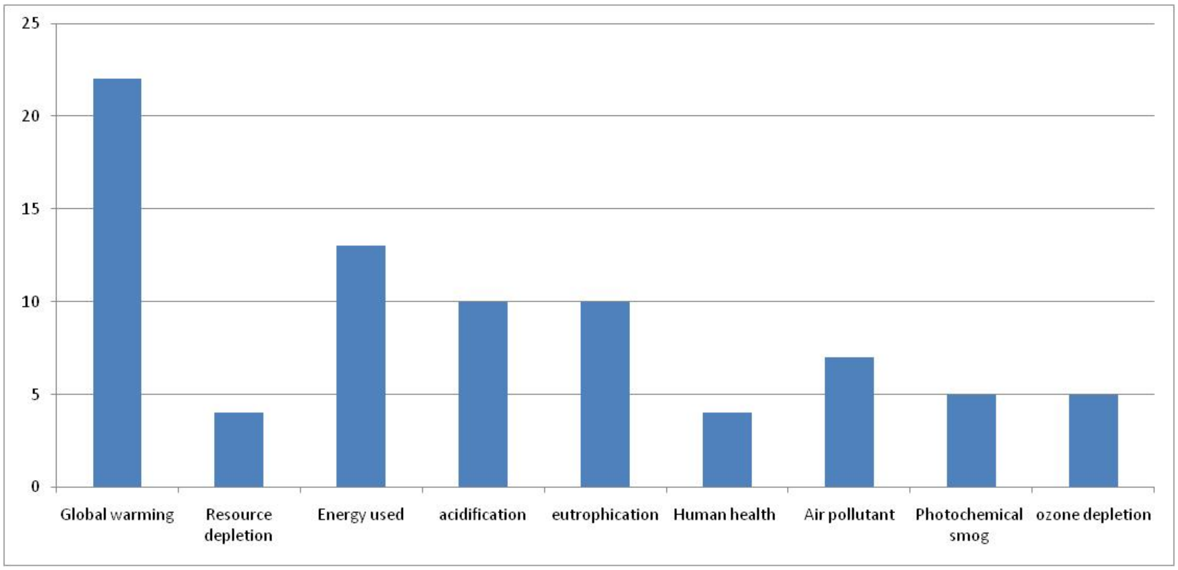

Figure2.10. Breakdown of LCA studies by field of used environmental impact categories

As it is shown, global warming is the most used impact category in reviewed ethanol LCAs. There are different ways of calculation for this impact. Some studies used carbon dioxide (CO_2), Nitrous oxide (N_2O), and Methane (CH_4) emissions for calculation of GHGs [44, 59, 60]. And some others calculated this impact category just based on CO_2 equivalent value [41, 52-54]. After GHGs category, energy balanced assessment is mostly used as an environmental impact. It does not have a common characterisation factor but it is seen as an environmental impact category. The calculation of energy used for process in reviewed studies can be based on either Joule [48, 60, 61]or BTU [62, 63].

Acidification and eutrophication are also presented in ten LCA studies out of twenty six. The impacts of acidification and eutrophication are mostly related to the nitrogen (and phosphorus) in the agricultural process such as feedstock cultivation.

c. Allocation

As mentioned before, the selection of how to decide what share of the environmental burdens of the activity should be allocated to ethanol and other co-products is allocation. According to the feedstock used in the process, various co-products are formed. For example, in the sugar cane-to-ethanol process, bagasse (fibre residue from extraction of sugarcane juice) is a co-production which can be used for electricity production. The types of co-products during corn-to-ethanol production depend on the milling system. In wet milling systems, corn syrup, corn oil, corn gluten meal, corn gluten feed and food-related products such as vitamins and amino acids can be produced. When dry milling of corn is used, animal feeds (distillers grains and soluble, DGS) are the potential co-products. For cellulosic feedstocks, electricity is the most common co-product of ethanol [1, 40, 51, 64, 65].

For ethanol LCAs, different allocation methods have been chosen under specific conditions and assumptions which are shown in the

Figure2. 11.

Avoiding allocation has different concepts such as system expansion, replacement and substitution. Among the reviewed LCAs, some used system expansion for avoiding allocation and some applied replacement concept in their studies [62, 66]. But these concepts cannot be distinguished firmly in practice so they are regarded as the same method in principle. As a result, the allocation procedures in this study are divided into three groups including avoiding allocation, physical and economical methods. Each of these methods has their advantages and disadvantages which are studied in the following.

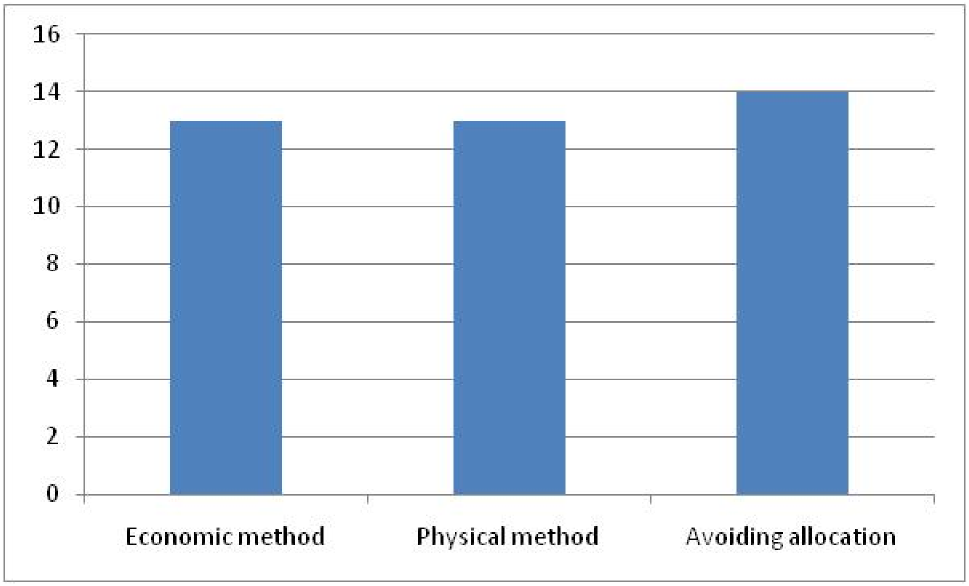

Figure2. 11. Varity of different allocation methods

According to Ekvall and Finnveden [2001], avoiding allocation procedure gives the chance to model the indirect effects [67]. This method can be also a good alternative when there is not reliable inventory data for products or when the market is restricted[68]. On the other hand, the appropriate results will be accessible when appropriate data for the indirect effects and functions are used [67]. When avoiding method is used, choosing the substitution products for co-products in the system should be as close as reality in order to have the same environmental burdens. For example DDGS is a co-product of ethanol production through dry milling process. In avoiding method, we need to identify a product which can be replaced by DDGS in order to estimate the environmental impacts of ethanol production. These substitution products are selected differently in different studies such as soybean meal [69], soybean oil[55] or corn/soybean meal[66]. But the quantity of both products have to be equal and if not, the correlation factor should use to make the function of both products equivalent[55]. So even with the same avoiding allocation method, results can be different based on the various assumptions or calculation method. As a result, using system expansion is complicate and time consuming as it is necessary to collect all accurate data for every sub-process in the system. Another difficulty of avoiding procedure is its complexity since it involves new sub-processes for every co-product.

Physical allocation by itself is divided into mass and energy methods. Mass allocation method frequently gives results but it is not always reasonable. For example assigning the majority of environmental impacts to the co-product which can be used somewhere else is not logical [39]. It cannot be also used for energy output in the system and it seems that simple mass allocation is not a good approach when the quantity of one co-product is far from another. In term of energy allocation, there were two different concepts in published LCAs including energy value [38, 55, 57] and energy consumed [63]. Generally physical allocation works well always when there is a close correlation between the physical property and the value of co-products [51-53, 56]. Another advantage of this approach is the opportunity of undependability to time.

In market value allocation the timeframe of the prices change the results of the assessments. But there is not one single method to monitor the influence and this uncertainty in the system. For example, when economic method is allocated for ethanol (main product) and animal feed (co-product), the price as the basic data for calculation is changing over time. Börjesson [2009] suggested using a data interval reflecting potential variation in prices as a solution. But it is also mentioned that the prices for ethanol and animal feed effected by the prices of feedstock and waste are relatively linked each other over time which make the based-economic calculation constant by time [68].

Generally, selection between two allocation methods, physical and economic, is highly depended on the type of feedstocks using for ethanol production. For example, when we are looking at ethanol production from grains, the energy contents in the form of straw is more than the energy contents in the form of ethanol but the economic value of straw is 10-15% of this value of ethanol. Nguyen and Gheewala [2008] have also the same discussion when comparing Cassava-based ethanol and gasoline. Although gasoline has higher energy contents but its octane value is less than ethanol. Consequently, it has less efficient thermodynamic operation in engines. This is the reason they chose economy allocation method to assess this study [70]. It is argued that economic allocation should be used in the systems with huge quantities of co-products with low economic value.

Some of LCAs avoid allocation procedure or use either economic or physical methods to show the influences of each of them for the final results [38, 39, 57, 59, 61, 62, 71]. According to Kim [2002], sensitivity analysis for ethanol production shows that choosing allocation methods have the most influences on the results in compare to any other parameters in ethanol production. It is shown that the difference in the net ethanol energy is changed around 30% by choosing different allocation procedures [55]. Malca and Freire [2006] also show in their study that results of LCA for wheat and sugar beet based-ethanol is highly sensitive to the allocation method [57]. The difference of energy renewability efficiency varies more than 50% for wheat based-ethanol. This value is less sensitive to allocation procedures for sugar beet based-ethanol as co-products are ignored in calculation. The same result is concluded in the study done by Bernesson et al. [2006]. It is argued that the results are depended on the allocation method of the environmental burdens between ethanol and by-product [38]. The other LCA study done by Hill, Nelson et al. [2006] introduced Net Energy Balance ration (NBE, energy output/energy input) for the sensitivity analysis. This amount is changed from 1.21 in economic allocation to 1.71 in physical allocation (energy content) for corn based-ethanol production with alternative co-products [66].

Although allocation methods are divided into specific categories, each allocation method has been applied differently by various practitioners. In other words, different assumptions and calculation methods can be applied which result in different outcomes even with the same allocation method.

There is a lack of explaining what the key factors are for selecting methodological choices in every situation. It is not logical to identify one single method for it as these choices are highly depended on the case study and the assumptions which are employed in the study. For this reason the methodological choices should be identified based on a ethanol case study.

Chapter 3- Methodology

3.1. Objectives and hypotheses

3.1.1. Main objective

The main objective of this study includes:

- To develop an LCA-based methodology appropriate for calculating the set of environmental metrics that describe the environmental performance of biorefinery, and to conduct the necessary analyses that show the conditions under which biorefinery scenario is environmentally preferable over other biorefinery scenarios

3.1.2. Specific objectives

The specific objectives of this study include:

- To assess the body of knowledge related to LCA studies for ethanol production using different feedstocks, in order to understand LCA-based approaches that have been used for allocating environmental burdens for evaluating ethanol biorefinery design alternatives.
- To identify a set of metrics that capture the most important environmental attributes of biorefinery processes in order to quantify the environmental impact of ethanol production.
- To apply an LCA methodology suitable for comparing the environmental impacts of ethanol production scenarios from different feedstocks by calculating and interpreting the selected set of environmental impacts using a case study basis.

3.2. Overall methodology

As mentioned, the purpose of this work is to develop an LCA methodology to evaluate the environmental performance of ethanol from different feedstocks. Figure3.1 shows the proposed methodology to address this problem.

The general methodology of this work includes three blocks.

The first block identifies the methodological choices, such as system boundary, environmental impact category and allocation procedure, that have been made in ethanol LCA studies. The consequences of these choices for ethanol production are evaluated in order to propose an appropriate LCA methodology. 26 LCA studies concerning the production of ethanol from different first and second generation feedstocks have been reviewed. A critical review of the strengths and weaknesses of different approaches was done to determine the consequences of these choices on the results, including system boundaries, allocation procedures and environmental impact categories in the respective LCA publications. To assess the performance of these different methodological choices in LCA, a base case was then defined. The base case enables the characterization of the methodological choices and comparison of different methods and their consequences for the results. This resulted in a proposed methodology for ethanol production based on the selected base case.

The aim of the second block was to complete a systematic review of environmental metrics that have been used for evaluating ethanol production, and to interpret these in order to arrive at a set of metrics that capture the most important environmental attributes of the ethanol biorefinery process. In this block, different ethanol production scenarios were selected. Flow charts and design data needed for the baseline scenario and the variants were defined in order to calculate the mass and energy balances for all processes. Then, LCA-base and other metrics were identified through a procedure for the baseline model. The data entered to LCA software was checked based on the baseline model and expanded to all scenarios later. Results were classified and characterized by LCA software automatically.

The last block included the interpretation of results, identification of key parameters and comparison of scenarios. The identification of key parameters results from the sensitivity and scenario analyses. At the end of this block which is the interpretation step of LCA, the opportunities to improve the environmental performance of ethanol production were identified for all scenarios.

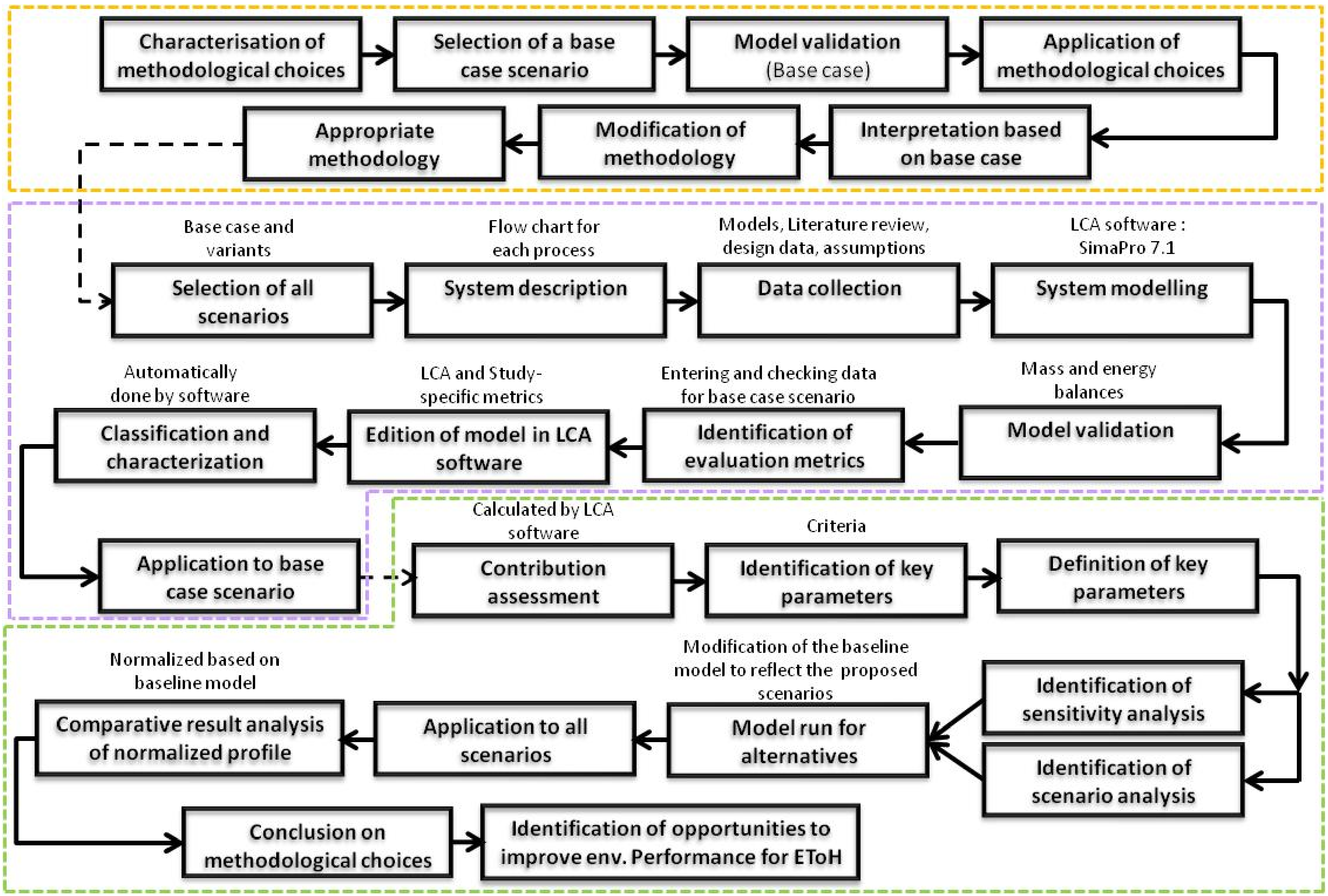

Figure3.1. General approach of the study

Chapter 4- Publication executive summary

4.1. Presentation of publication

The following paper, that was submitted to the scientific journal, is included in appendix A of this thesis:

- "Comparative life-cycle assessments for different feedstocks-to-ethanol production", M. Ranjbar and P. R. Stuart, 2009, *Submitted to PAPTAC*

The aim of this paper is to compare the environmental advantages and disadvantages of ethanol production from different feedstocks including woodchips, hemicelluloses and triticale straw. In order to compare the environmental performance of ethanol production from mentioned feedstocks, an LCA_based methodology was developed by assessing a body of knowledge related to ethanol LCA studies to identify some of the methodological choices and their consequences in the final result. This assessment is included in appendix D.

4.2. Synthesis

4.2.1. Development of methodology

As mentioned in the methodology, the first step of this research is to propose an appropriate LCA-based methodology. In order to access this objective, following works are done.

4.2.2. Characterization of methodological choices

According to literature review, methodological choices such as system boundary, set of environmental impacts and allocation procedure are critical selections for an appropriate LCA methodology. There is general acknowledgment that methodological choices should be made in relation to the goal and scope of the study. These selections in LCA are relevant to different applications. For this reason, a base case is selected in order to apply different methodological choices and characterize the best methodology for that baseline model. The base case study is explained in details in the following.

4.2.3. Exploration of the methodological choices

The selected base case study was done by Kemppainen et al. [2005] [51] and the model used in this study was developed based on the mass and energy balances done by National Renewable Energy Laboratory (NREL) [17].

This ethanol production process includes dilute acid prehydrolysis, simultaneous saccharification and fermentation and cellulase enzyme production sections. It begins by feed handling section, where the chips are washed and reduced in size. Then hemicellulose sugars are released by using dilute acid hydrolysis in pre-treatment area and the hydrolazate stream is split to the fermentation step. The cellulase enzymes are produced in cellulase enzyme production area and sent to fermentation reactors for ethanol production. The produced ethanol is purified by distillation and stored in the storage area. There is also waste water treatment section in order to treat the bottom streams of distillations. The recovered water is recycled back to the process and the solid from waste water treatment process and produced biogas are burned in a combustor in order to provide the steam and electricity needed in the plant. In other words, this process is energy self-sufficient and the excess electricity is sent for sale to the grid [51].

In this study the assumed feedstock is woodchips which was used in the LCA study by Kemppainen et al. [2005] and no change in the mass and energy balance (NREL simulation result) is considered. The components of feedstock for the ethanol process are shown in Table4.1.

Table4.1. Composition of feedstock for ethanol process [Kemmpainen et al., 2005]

Component	% Dry wt basis
cellulose	49.15
xylan	16.89
arabinan	1.04
mannan	3.76
galactan	1.01
acetate	3.38
lignin	24.45
ash	0.31
moisture	68.4

The feed rate of 83333 kg/h of dry biomass is assumed. This amount of feedstock is supposed to be sufficient for production of 60 million gallons of ethanol per year.

Data in this study were collected from a variety of sources including literature, reports and some directly from the used tool SimaPro 7.1, Ecoinvent inventory database. The Life Cycle Inventory Assessment (LCIA) method that was used is impact 2002+. Other data on transport, ethanol process and electricity production are obtained from NREL report [17]. The mass and energy balances of this ethanol case study are summarized in Table D.3 in Appendix D.

These balances were manually input into SimaPro software to estimate the environmental impacts of the woodchips-to-ethanol process.

4.2.4. Application of LCA methodology

The first step of each LCA study, goal, is defined as "to compare the environmental performance of ethanol production from woodchips as a regional cellulosic feedstock based on different LCA methodologies". In order to compare the consequences of different methodological choices, various selections are applied in the model and characterized as following:

a. System boundary

The model was expanded to include all important activities as shown in Figure 4.1.

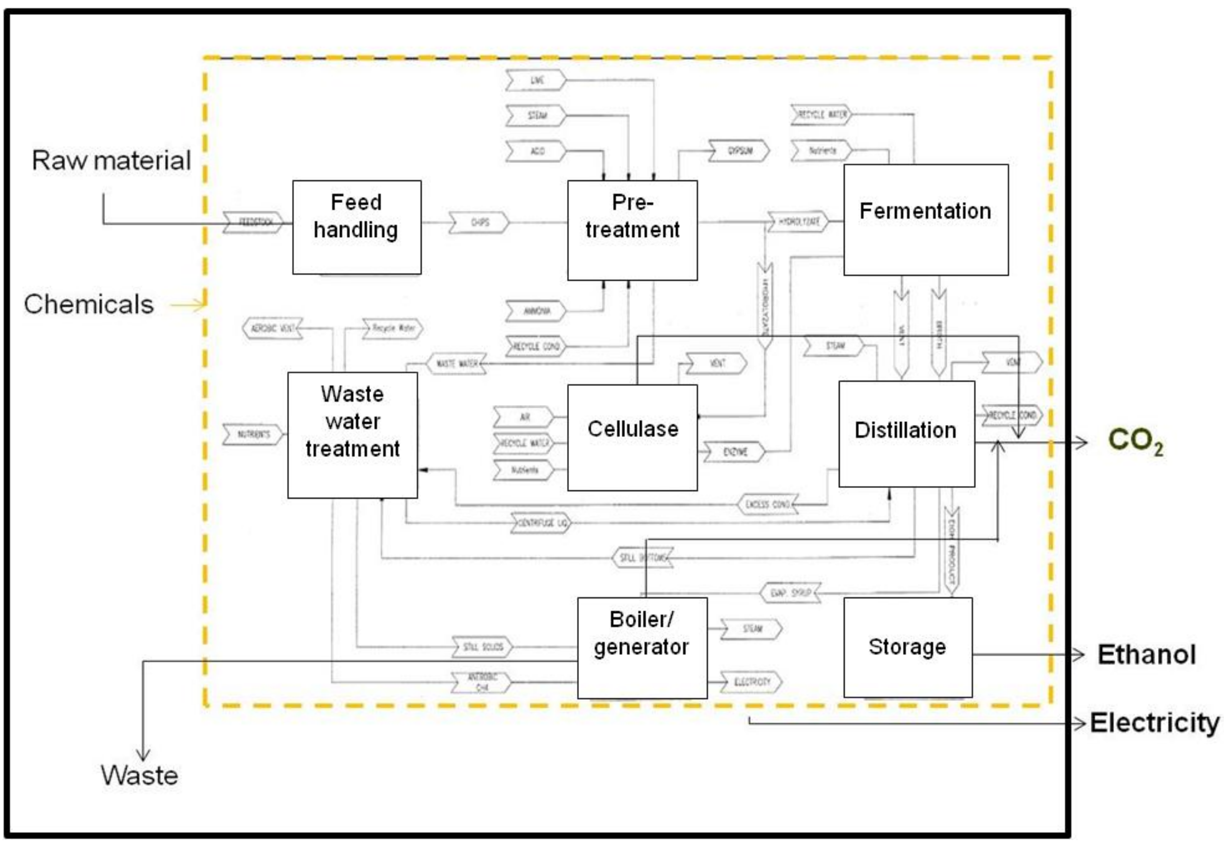

Figure 4.1.System boundary and flows for the overall LCA

The model was expanded to include all activities that would be affected by a change in the system. It starts with the cultivation of raw material, transportation to the mill, conversion of raw material to ethanol and finally ethanol production. The treatment of wastes, the production of chemicals and electricity needed for the process are also accounted in the system. But the question in the ethanol LCA is what the environmental consequences of including the usage phase are in the system? The end-use combustion phase in vehicle can be excluded from the boundary as it is always the same in ethanol fuel production. Besides, a long chain in the ethanol LCA study decreases the chance to describe a status-quo situation and hot-spot identification in order to recognize a number of improvement options. As a result, cradle-to-gate is selected as the suitable system boundary of our model.

b. Environmental impact category

The terms of impact category (midpoint) and damage category (endpoint) refer to the level within the environmental mechanism at which the respective effects are characterized. In order to select the most appropriate set of environmental indicators, we applied two different methods in the base case. These methods are summarized in the following table.

Table4.2.System boundary and flows for the overall LCA

Methodological choices	Method I		Method II	
System boundary	Cradle-to-gate		Cradle-to-gate	
Environmental impact category	Damage category	Human health, Ecosystem quality, Climate change, Resources	Impact category	Human toxicity, respiratory effects, ionizing radiation, ozone layer depletion, photochemical oxidation, aquatic ecotoxicity, terrestrial ecotoxicity, terrestrial acidification, aquatic acidification, aquatic eutrophication, land occupation, global warming, non-renewable energy, mineral extraction
Allocation procedure	Energy allocation		Energy allocation	

According to the table, the two selected methods have the same system boundary which is cradle-to-gate. The reason of this selection is discussed in the previous section. In term of allocation procedure, energy allocation is selected for both methods. This enables us to characterize the consequences of different environmental impacts (endpoint vs. midpoint) in the result. By applying method I and II in the base case, the following results are obtained as shown in the

Figure 4.2 and

Figure 4.3.

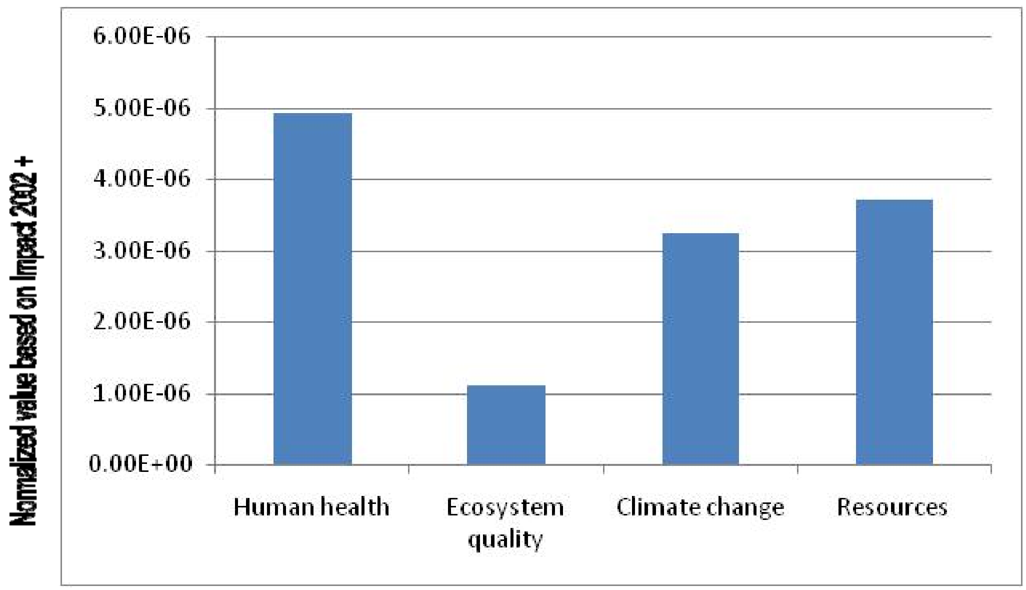

Figure 4.2. Damage category (Endpoint)

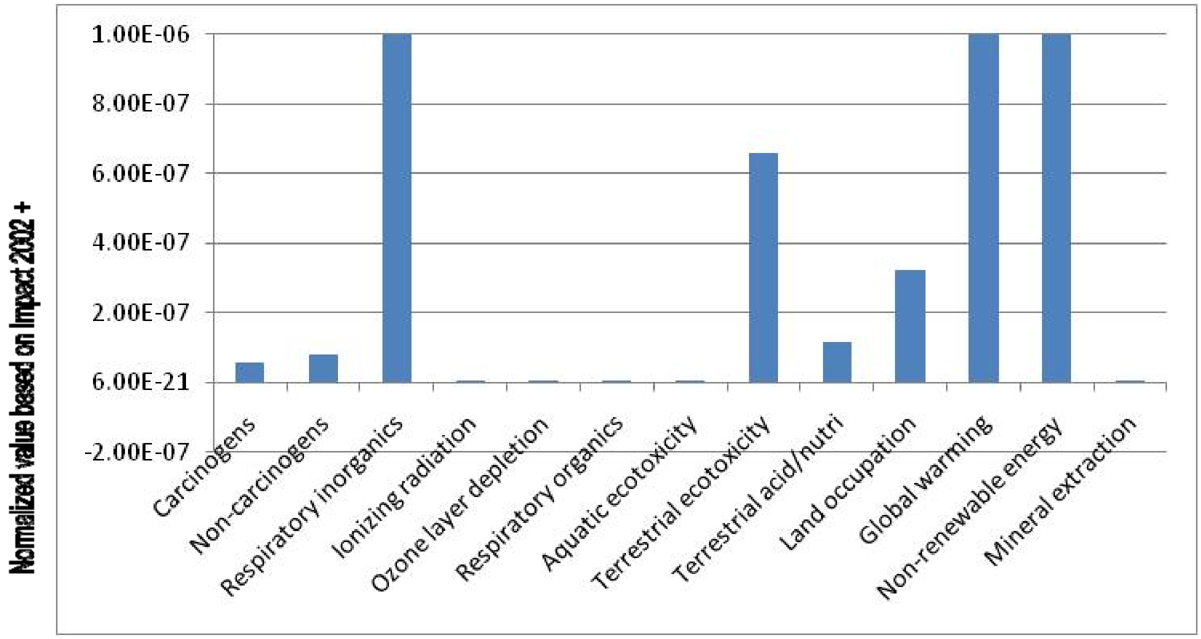

Figure 4.3. Impact category (Midpoint)

As shown in the

Figure 4.2, endpoint level is more understandable. On the other hand, it is not obvious which effects or assumptions are taken into consideration in endpoint level. This decreases the transparency of the LCA study. For example, ecosystem quality (

Figure 4.2) is caused by aquatic and terrestrial acidification, ecotoxicity and land use (

Figure 4.3). But it is not clear which of these impacts are brought into the account. This arise more uncertainties in the results. Besides, the midpoint impacts are taken directly from the inventory and they are determined directly over a certain area. This lack of adequate scientific information leads us to select the midpoint level as an appropriate environmental category for this base case.

c. Allocation procedure

As discussed before, allocation procedure is one the key point which brings uncertainty into the assessment when there is more than one product in the system. According to ISO standard "The allocation should be avoided. Where allocation cannot be avoided, the inputs and outputs of the system should be partitioned between its different products or functions in a way that reflects the physical relationships or other relationships between them.” [67] . Following the ISO guideline, avoiding allocation is selected in the first step in order to assess its consequences on the results. If the avoiding allocation is not applicable, environmental impacts should be divided between ethanol and electricity in the physical or other relationships. In order to characterize and determine a better method, both system boundary and environmental impact category are fixed for the systems and two allocation procedures are applied. Table4.3 shows the methodological choices selected for the study for two methods.

Table4.3. Characterization of allocation procedure

Methodological choices	Method I	Method II
System boundary	Cradle-to-gate	Cradle-to-gate
Environmental impact category	Midpoint (Impact category)	Midpoint (Impact category)
Allocation procedure	Avoiding allocation	Physical allocation

In method I, we expand the boundaries of the system to include all the activities outside of the production of ethanol. In method II, environmental impacts of the whole system are divided between ethanol and electricity based on the energy content. The results are two methods are shown in the Figure 4.4.

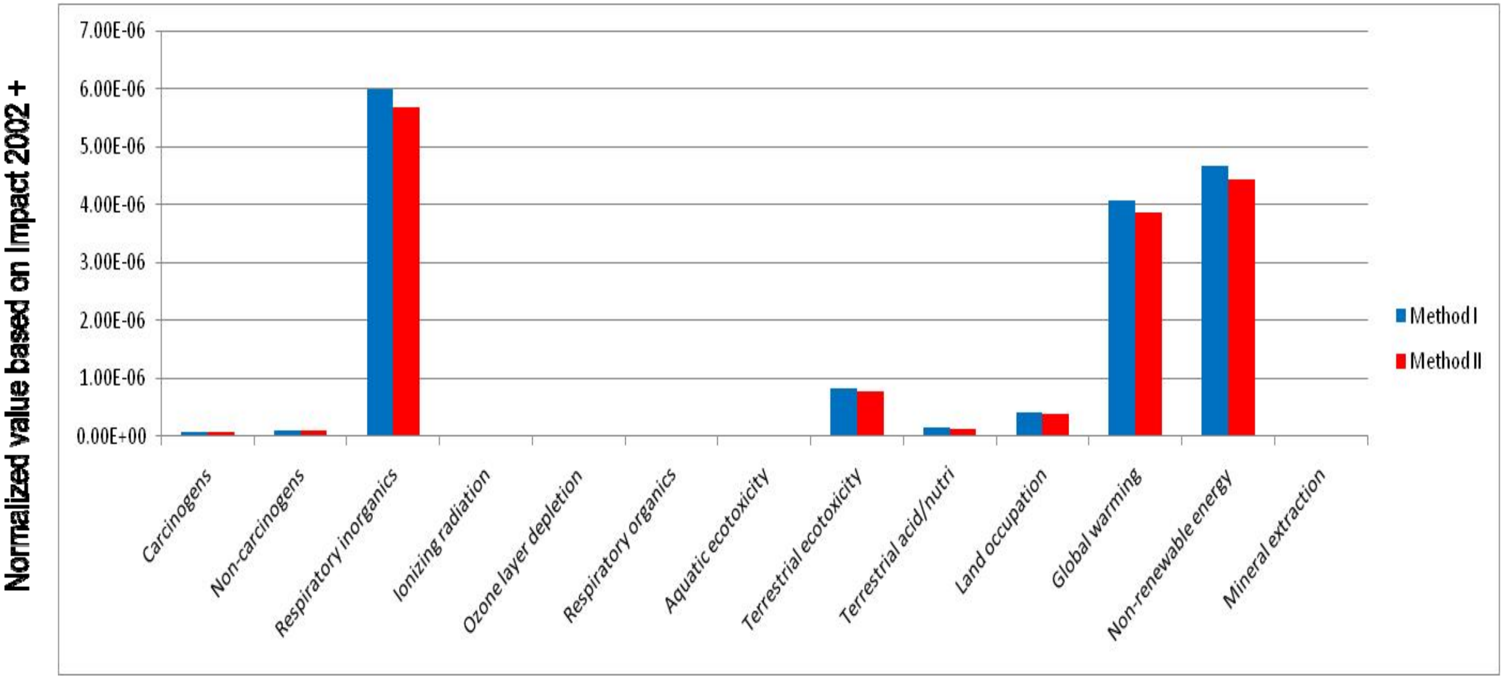

Figure 4.4. Characterization of allocation procedure

As it is shown, the results from method II (physical allocation) are less that the results from method I (System expansion). This reduction is obtained because of the partitioning and distribution of environmental impacts allocate to the electricity. This part is the number which used for allocation and the amount of this could be different based on different assumptions. To avoid this uncertainty, it is suggested to avoid allocation in order to have the overall emissions of the whole system. In this method all activities are also accounted in the model and it is closer to the reality. As a result the appropriate procedure for this base case is avoiding allocation which also suggested by ISO standard.

4.2.4.1. Discussion

According to characterization of methodological choices in the previous sections, the most appropriated method for this specific study of woodchips-to-ethanol production is selected and summarized in the following table.

Table4.4. Selected methodological choices for the specific base case of ethanol production

Methodology	Selected method
Goal	To compare the environmental impacts of ethanol production from upper Michigan timber based on the most appropriate LCA methodological choices
System boundaries	Cradle-to-gate
Functional unit	1 MJ of ethanol + 2.3*10e-3 MJ of electricity
Allocation approach	Avoiding allocation/ System expansion
Environmental impact indicators	Human toxicity, respiratory effects, ionizing radiation, ozone layer depletion, photochemical oxidation, aquatic ecotoxicity, terrestrial ecotoxicity, terrestrial acidification/nutrification, aquatic acidification, aquatic eutrophication, land occupation, global warming, non-renewable energy, mineral extraction
LCIA method	Impact 2002 +

While the selection of the methodological choices will affect the results because of fundamental differences in modeling, the choice of a normalization reference aims at better interpreting the results, which is critical if LCA is to be used for practical decision-making. Normalization should be applied in order to determine which environmental impact is more significant in ethanol production. The normalization approach should fulfill the horizon of the study. Norris [37] discussed the internal and the external approaches for normalization in LCIA. In internal approaches, the score of a particular category is divided by a function of the values obtained for the studied alternatives for that category. External approaches are generally linked with the contextual view in which the relative significance of results in different impact categories is assessed. External normalization allows the evaluation of the relative significance of a category's result to the global impact of a chosen referential system. This system should be justified based on the geographical location and the technical characteristics of installation. As sugar and starch for ethanol have been until now the primary raw materials, the technology for first generation of ethanol production is completely well known. In order to make a good judgment between different types of feedstocks for ethanol production, in our case woodchips-to-ethanol, the corn-to-ethanol process is selected as the referential system. This enables us to compare the environmental impacts of a second generation ethanol based on the first generation process.

According to this approach, the significance of environmental impacts can be calculated according to the following equation where; Ni is the normalized environmental performance, $I_{i,case}$ is the characterization results for woodchips-to-ethanol production and $I_{i,RS}$ is the characterization results of referential system.

$$\mathrm{Ni} = \frac{\mathrm{Ii, case} - \mathrm{Ii, RS}}{\mathrm{Ii, case}} \qquad \text{(Equation 1)}$$

In this approach, change is compared to the total improvement when implementing the corn-to-ethanol production as referential system. This difference is divided by the initial performance of the system. A positive result means that the alternative performs worse than the referential system, while a negative result means that it performs better.

The results of external normalization are shown in

Figure 4.5.

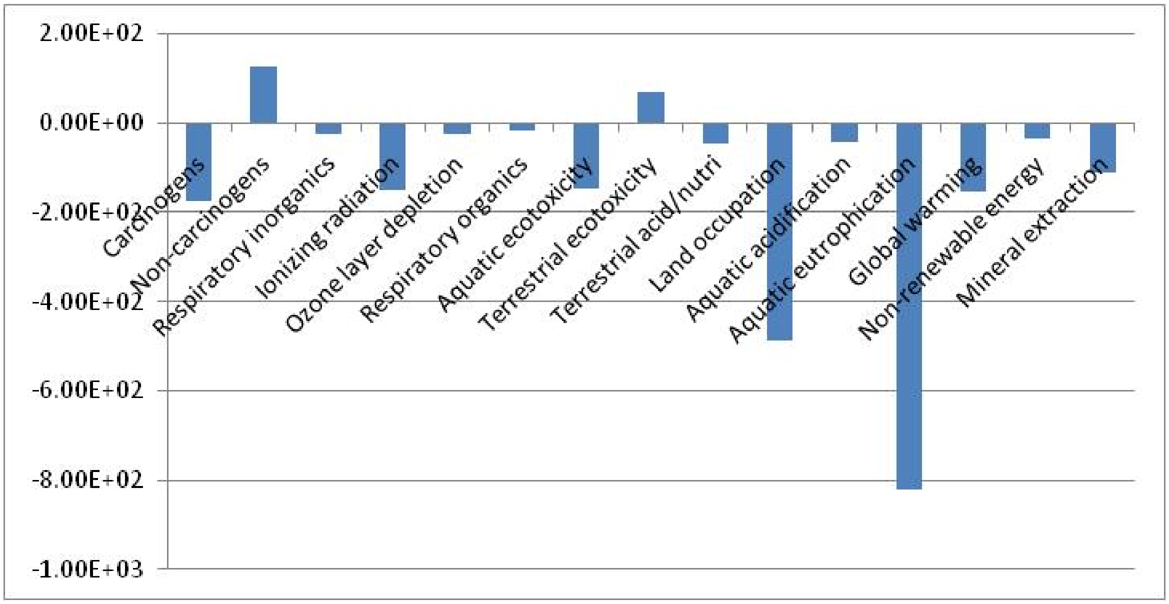

Figure 4.5. Normalized environmental indices for the timber-to-ethanol production

Based on the methodological choices selected in this paper, the conversion of biomass to ethanol is a potential fuel for transportation. As it is shown, the production of ethanol from woodchps has a better environmental performance in most of the impact categories. For example, the obtained result for eutrophication shows a very good environmental advancement when ethanol is produced from timber in compare to corn-based ethanol. This effect is mainly because of emissions associated with corn cultivation. Land use and aquatic ecotoxicity are two other categories with more friendly environmental impacts for woodchips to ethanol based on the normalization method. In term of land use impact, farming of first generation feedstock for ethanol production define environmental performance of the timber to ethanol better, when there is no need for cultivation of second generation ethanol.

In the case of non-renewable energy for the production, the reduction of using fossil fuels is resulted.

Only two impact categories, non-carcinogens and terrestrial ecotoxicity impacts, show worse environmental performance. With respect to these impacts, they refer to the impact of heavy metals specifically Zinc and Copper emitted to the soil and air ecosystem. According to the Ecoinvet report, these are listed as emissions from combustion using diesel and petrol in the process and their main significant effects are associated with terrestrial ecotoxicity and non-carcinogens[72].

By the end of this section, the first building block of methodology, selection the most appropriate methodological choices for ethanol production, is done. To start the second step, different ethanol scenarios should be defined in order to collect all needed data. This step is explained in the following section.

4.2. 5. Ethanol Biorefinery scenarios for LCA evaluation

Three different feedstocks are selected for this study including triticale straw, woodchips and hemicelluloses. Triticale is adapted widely in western Canada as a local biomass as a result; it could be a reasonable source for ethanol production. Woodchips is another opportunity for ethanol production as it is currently used in pulp and paper mills in Canada. This selection enables us to compare the environmental impacts of ethanol production stand-alone and in IFBR. Figure 4. 6 shows the different biomass sources and processes employed in this study. each process is explained in details in the following section.

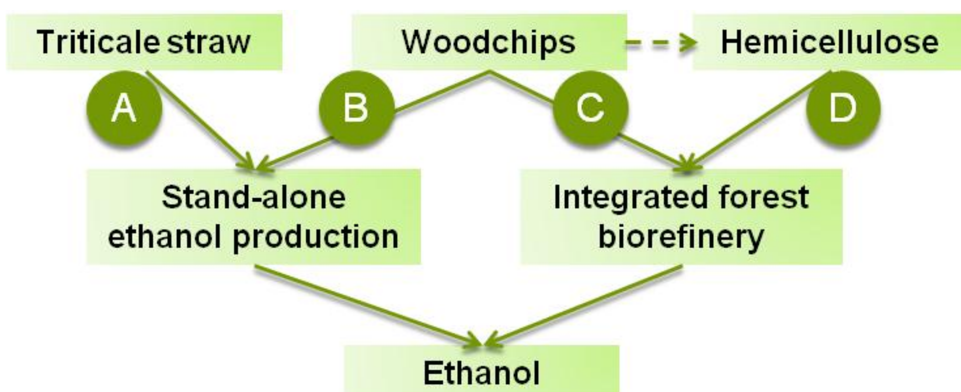

Figure 4. 6. Different biomass and pathways employed for comparison

4.2.5.1. Different ethanol process description

4.2.5.1.1. Triticale Straw (Greenfield)

Pathway A shows the conversion of triticale straw to ethanol. The process data employed this pathway is based on the process simulation done by NREL (National Renewable Energy Laboratory). This ethanol production process includes the prehydrolysis, simultaneous saccharification and fermentation and cellulase enzyme production sections. It begins with a feed handling section, where the raw material are washed and reduced in size. Then hemicellulose sugars are released by using dilute acid hydrolysis in the pre-treatment area and the hydrolazate stream is split to the fermentation step. The cellulase enzymes are produced in the cellulase enzyme production area and sent to fermentation reactors for ethanol production. The produced ethanol is purified by distillation and stored in the storage area. There is also the waste water section which treats the bottom streams of distillations. The recovered water is sent back to the process and the solid from process and biogas are burned in a combustor in order to provide the steam and electricity needed for the plant. In the other word, this process is energy self-sufficient and the excess electricity as the co-product is sent to the grid for sale [17]. In order to produce the heat process and electricity as a co-product, a burner, boiler and turbogenerator system is defined for the plant. All of the lignin, some of the cellulose and hemicelluloses from the feedstock remained unconverted is used in this section. The biogas high in methane from anaerobic and sludge from aerobic digestion are also burned to generate steam and electricity for the process. The flowchart and details of this process is available in appendix B.

A multistage turbine and generator showed in Figure 4.7 are used to generate electricity. Steam is extracted from the turbine at 3 different conditions for injection into the pre-treatment reactor and heat exchange in distillation and evaporation. The remaining steam is condensed with cooling water and returned to the boiler feed water system along with the condensate from the various heat exchangers in the process. Treated well water is used as makeup to replace steam used in direct injection. Sulfur dioxide, carbon monoxide and NOx is generated during this process [17].

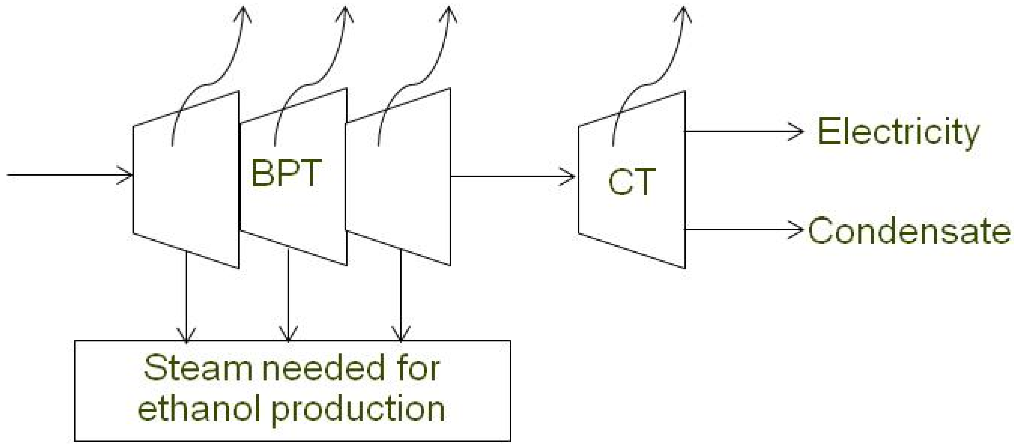

Figure 4.7. A multistage turbine and generator used for electricity production [Wooley et al.]

4.2.5.1.2. Woodchips (Greenfield)

This pathway (B) is also the same as pathway A but with the different feedstocks which is woodchips. This process data employed in pathway B is also based on the process simulation done by NREL [17]. This process was explained in details in the previous section.

4.2.5.1.3. Woodchips (Retrofit)

Process C is a novel use of two processes, the first of which provides ethanol (main product) and energy (co-product) in the form of steam. This steam is then sent to the pulp mill in order to provide the additional energy required for the pulping by changing the type of generator used in the ethanol mill. The careful management of the extent to which the fuel resource is used in a pulp mill may actually reduce the amount of purchased energy provided by fossil fuels. The concept of ethanol production is the same as woodchips-to-ethanol explained in the previous sections [17]. Pulping process includes receiving, debarking and chipping the logs. These are mixed in the reactor with the pulping chemicals. The pulp produced is washed with water. The next steps include bleaching and drying. In addition to the fiber line it has pulp procession operations for removing shives or uncooked pulp, cleaning and screening operations for removing impurities in the pulp, and processes for recovery of the energy content in the dissolved wood solids. Besides, the pulping chemicals are regenerated from the spent liquor stream. It is assumed that the steam needed for the mill is produced in-site but the energy used in lime kiln is produced from natural gas. This Kraft pulp mill is explained previously in the section 2.2.1. [22, 25]. More data for this process and its flowchart is available in Appendix B.

4.2.5.1.4. VPP (Retrofit)

Pathway D or Value Prior Pulping (VPP) includes the "near-neutral" hemicellulose pre-extraction integrated into an existing hardwood Kraft mill. This process starts with wood extraction for hemicellulose removal, flashing of the extract to produce steam, recycling a portion of extract back to the extraction vessel in order to raise the solids content of the extract, sulphuric acid hydrolysis for conversion of carbohydrates into mono sugars, filtration to remove lignin, liquid-liquid extraction, distillation to remove acetic acid and furfural followed by a liming step, fermentation of sugars for ethanol production and finally distillation of product[25]. It is assumed that the existing Kraft pulp mill produces market pulp as well as ethanol and acetic acid using the hemicellulose extraction process. By integration of the VPP process into this existing pulp mill, less white liquor is required in the cooking step. This will result in a corresponding decrease in the amount of calcium carbonate ($CaCO_3$) that has to be removed in the white liquor clarifier and decomposed to lime in the kiln. This reduction in flow of $CaCO_3$ has a significant effect on the amount of energy required to operate the lime kiln because the hemicellulose extraction process uses green liquor (Na_2CO_3 and Na_2S) as the solvent and the green liquor does not go to the causticization and lime cycles. Since in the near neutral hemicellulose extraction process less lime mud goes to the kiln, there will be a savings of fossil fuel consumption. The detailed mass and energy balances for these scenarios are explained in appendix B [22, 25].

4.2.5.2. Base case scenario and variants

In order to compare ethanol production from different feedstocks, base case scenario and variants should be identified. The selected scenarios for this study are different in the term of feedstock, process and co-products. As a result, selection of a base case scenario helps to evaluate the LCA results, calculate the evaluation

4.2.5.2.1. Base case scenario

The VPP process is selected as the base case scenario because there are more co-products produced in this process than others. The co-products in this process include pulp, electricity and acetic acid. This gives the opportunity to expand the system boundary for all other scenarios in order to have the same baseline comparison. Simplified representation of the VPP process is illustrated in Figure 4.8.

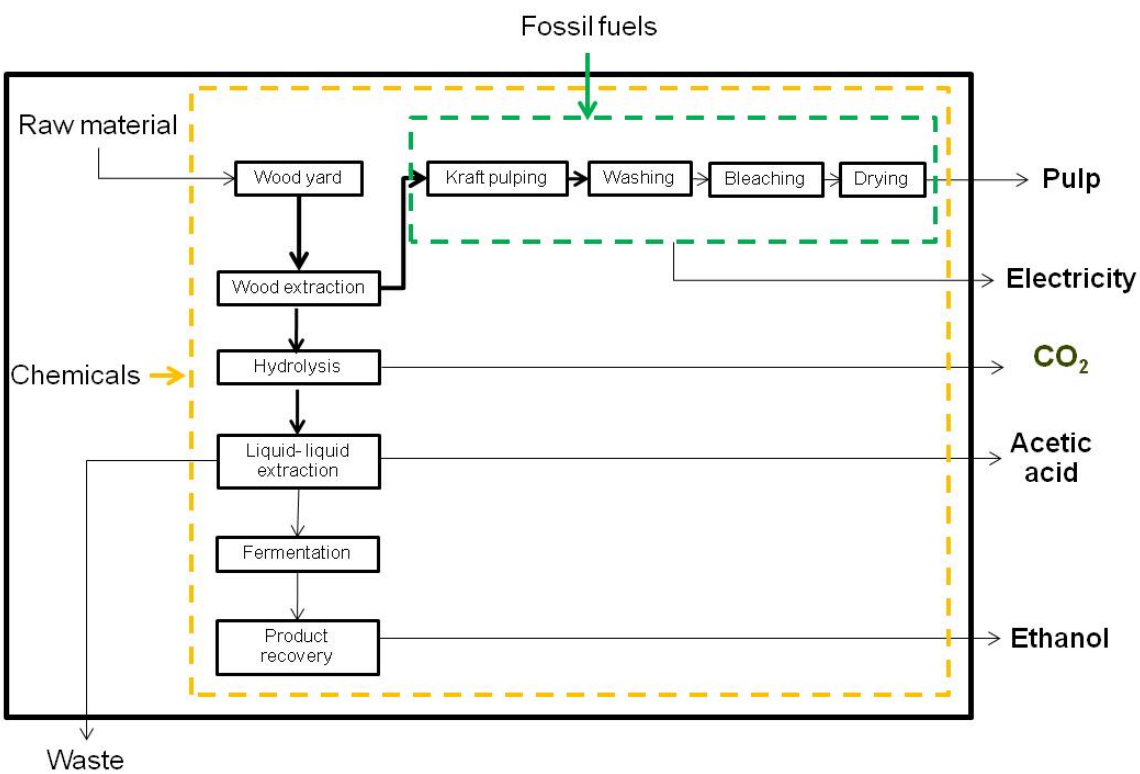

Figure 4.8. Simplified representation of VPP process

4.2.5.2.2. Variants

Other scenarios including triticale straw and woodchips through greenfield and retrofit pathways are selected as the variants in this study. The simplified representations of these scenarios are illustrated in the following.

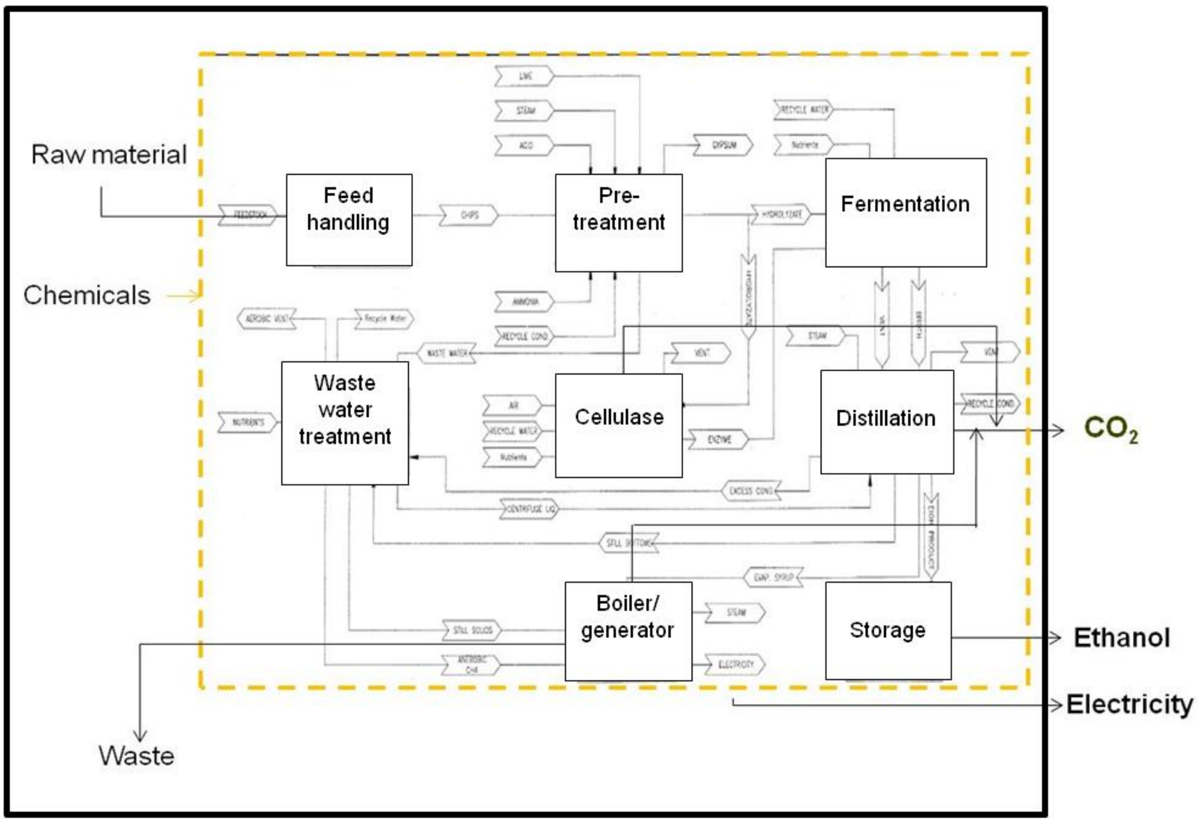

Figure 4.9. Simplified representation of greenfield pathways (Triticale straw and woodchips)

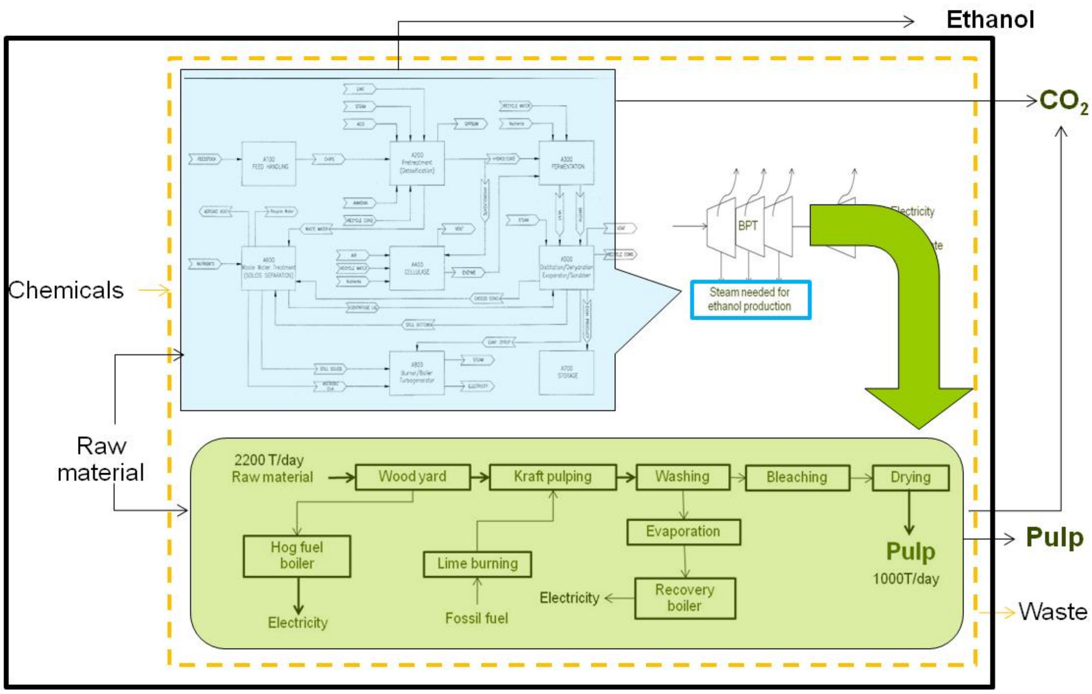

Figure 4.10. Simplified representation of retrofit woodchips-to-ethanol pathways

4.2.6. Selection of environmental evaluation metrics

According to the methodology, the third section includes Impact Assessment. In this section, it is important to identify the metrics which are used for the evaluation of LCA results. The development of metrics that relate environmental performance for production processes is an excellent way to begin the goal of sustainability into decision-making. This is a major challenge and there is a clear need for this area.

It is important that the metrics designed for the evaluation of a process production have the following characteristics among others [73]:

- Interpretable
- Rigorous scientific and technological basis for biorefinery pathways
- Understandable to a broad audience
- Highlight the process impact within the product chain
- Environmental hotspot analysis of a single biorefinery process, and/or for comparison between different biorefinery processes

In order to employ the suitable metrics, it is essential to develop the framework. In this study the framework is designed based on the target which is the comparison of environmental performance of ethanol production through different processes. The methodology for selection of environmental evaluation metrics is shown in Figure 4.11.

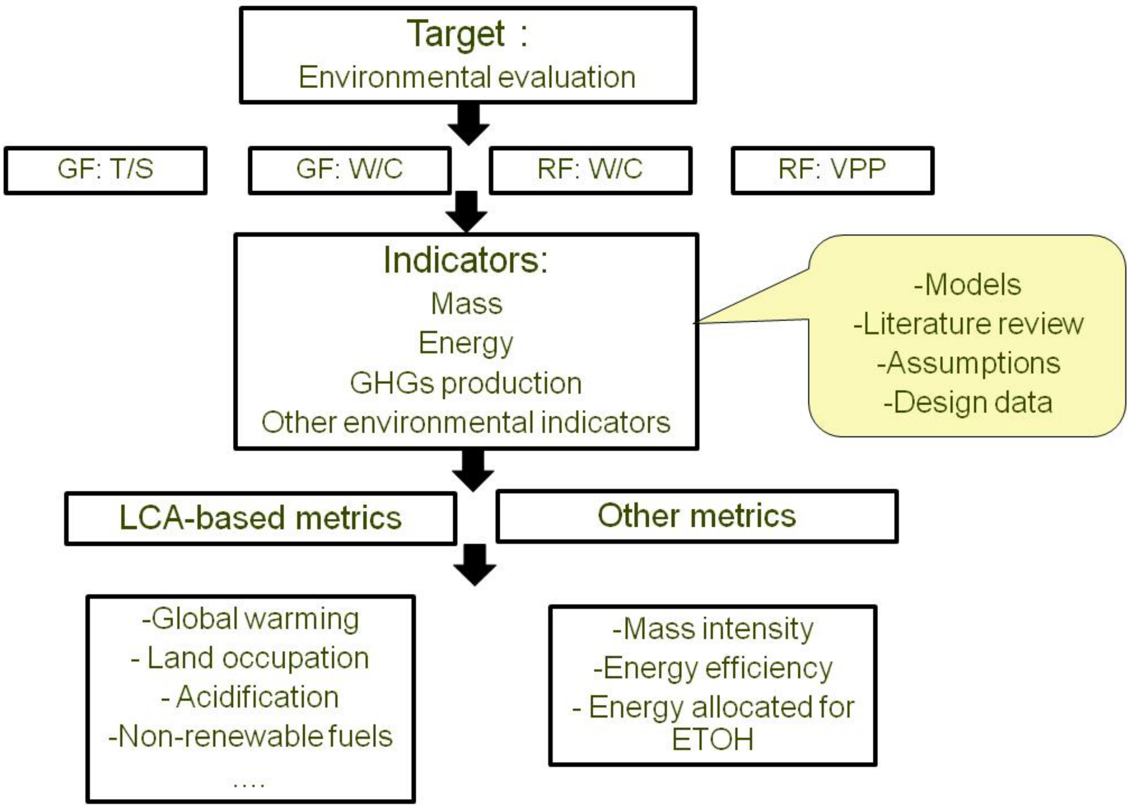

Figure 4.11. Methodology for selection of environmental metrics

As shown, different indicators should be chosen under the term of the target and according to the models, literature review, assumptions and data design in the study. The identification of these indicators guides us to select the evaluation metrics including "LCA-based metrics" and "other" metrics.

4.2.6.1. LCA-based metrics

This group of metrics should be selected under the term of goal and scope in the assessment. Most of the LCAs include energy consumption and CO_2 emission indicators in their study but few of them use other indicators such as terrestrial organics and inorganics potential, eutrophication potential, ozone depletion potential and various toxicity potentials [74].

The LCIA method used in this study is impact 2002$^+$. This method proposes a feasible implementation of a combined midpoint/ damage approach, linking all types of life cycle inventory results via 14 midpoint categories to four damage categories [75]. Overall scheme of this method is illustrated in Figure 4.12.

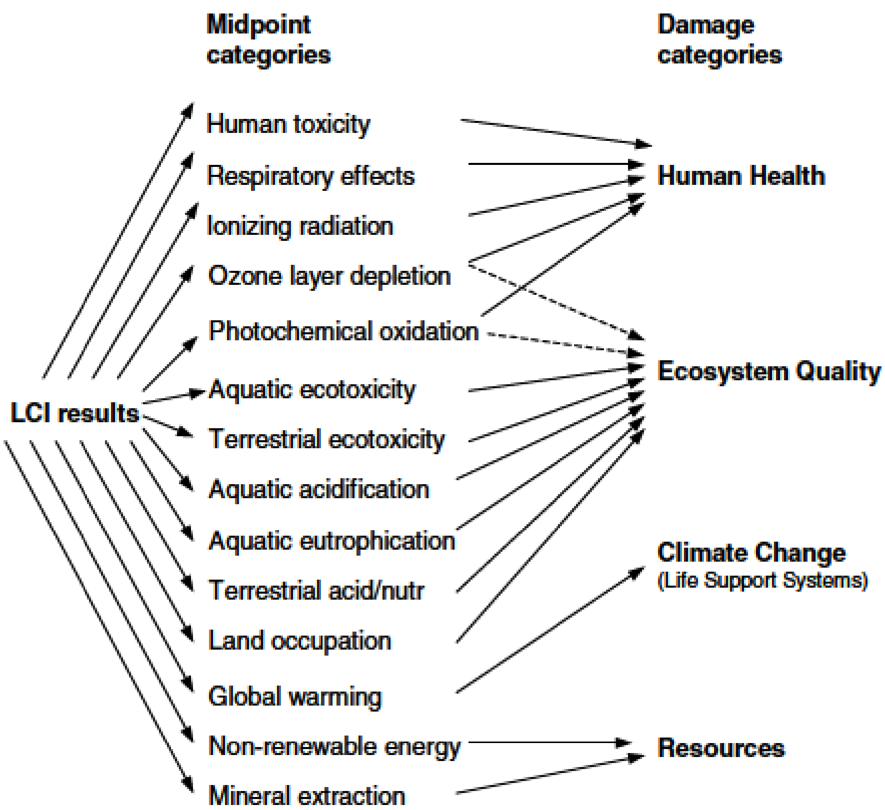

Figure 4.12. Overall scheme of the IMPACT 2002+ framework (Jolliet et al, 2003)

In method Impact 2002$^+$, midpoint characterization factors are based on equivalency principles, i.e. midpoint characterization scores are expressed in kg-equivalents of a substance compared to a reference substance. Table4.5 shows the reference substances and damage units used in Impact 2002$^+$ [75].

Table4.5. Midpoint reference substances for Impact 2002^{+}(Jolliet et al, 2003)

Midpoint category	Midpoint reference substances	Damage category
Human toxicity (Carcinogens and non-carcinogens)	Compounds toxic to Human health (Kg_{eq} Chloroethylene into air)	Human health
Respiratory inorganics	Compounds toxic to Human health (Kg_{eq} PM2.5 into air)	Human health
Ionizing radiation	Compounds toxic to Human health (Bq_{eq}Carbon-14 into air)	Human health
Ozone layer depletion	Chloroflurocarbons, Volatile organic compounds (Kg_{eq} CFC-11 into air)	Human health
Respiratory organics	Kg_{eq} Ethylene into air	Human health
		Ecosystem quality
Aquatic ecotoxicity	Toxic compounds released into aquatic ecosystem (Kg_{eq} Triethylene glycol into water)	Ecosystem quality
Terrestrial ecotoxicity	Toxic compounds released into terrestrial ecosystem (Kg_{eq} Triethylene glycol into water)	Ecosystem quality
Terrestrial acid/nutri	Kg_{eq} SO2 into air	Ecosystem quality
Land occupation	Land occupation and transformation, Loss of biodiversity (M^2_{eq} organic arable land-year)	Ecosystem quality
Aquatic acidification	So_x, No_x and NH_x (Kg_{eq} SO_2 into air)	Ecosystem quality
Aquatic eutrophication	Nitrogen and phosphorus (Kg_{eq} PO_4 $^{-3}$ into water)	Ecosystem quality
Global warming	Greenhouse effect gases -CO_2, CH_4, CO and No_x (Kg_{eq} CO_2 into air)	Climate change
Non-renewable energy	Depletion of fossil fuels (Kg_{eq} crude oil)	Resources
Mineral extraction	Depletion of minerals (Kg_{eq} iron)	Resources

Based on the environmental load summarized in Table4.5, consideration of energy and CO_2 emission indicators is a good possibility in this study to assess the reduction of GHG emission and energy consumption for different ethanol production from woodchips and energy crop as the pre-manufacturing of these feedstocks are different. Besides GHG emissions and energy, other environmental impacts can arise from feedstocks, production and processing of ethanol, the corresponding effects on water and soil quality should be considered.

These metrics depend on various factors including feedstock, cultivation practice, land management and downstream processing route. In all scenarios used in this study, pre-manufacturing is important for the environmental loads of toxic compounds for human health. Felling, skidding, transportation and chipping for trees and cultivation, collection, baling and loading for triticale straw result in $PM_{2.5}$ formation (Particle matter which is a mixture of solid particles and liquid droplets in the air) because of fuel combustion in vehicles and in industrial facilities. These activities also realise toxic compounds into the ecosystem such as water. As a result, respiratory inorganics (Human health) and terrestrial ecotoxicity (ecosystem quality) are selected as potential metrics for the environmental evaluation in this study.

Land occupation is also important because of different feedstock used for ethanol production have different quantity of arable lands. This methodology helps to identify the LCA-based metrics used in this study. Note, the selected metrics (Table4.6) has the most contribution among other midpoint categories when the LCA results are presented in damage category.

Table4.6. Selected LCA-based metrics

Midpoint category	Damage category
Respiratory inorganics	Human health
Terrestrial ecotoxicity	Ecosystem quality
Land occupation	Ecosystem quality
Global warming	Climate change
Non-renewable energy	Resources

4.2.6.2. Other environmental metrics

These metrics are the alternative selections which are depending on the goal and scope of the study whether the appropriate data are available. They are also justified because they are defined globally and accepted internationally. The selected metrics include mass intensity, energy efficiency and energy allocated for ethanol.

The definition and justification for these choices are summarized in Table4. 7. All the evaluation metrics include cradle-to-gate environmental life-cycle inventories.

Table4. 7. Selection and justification of metrics

Metrics	Definition	Justification
Mass intensity*	Mass of raw material converted to the products	Appropriate to the topic of study (Under the term of goal and scope) Appropriate data are available Defined globally and accepted internationally
Energy efficiency	MJ products/ MJ (Biomass + fossil fuels**)	
Energy allocated for ETOH	MJ fossil fuels**/ MJ ETOH	

*Mass intensity is not valid for electricity

**Fossil fuel used in both pre-manufacturing and manufacturing steps

Material intensity is expressed as quantity of materials which are converted to the products per unit output. This metric is calculated according to the mass of raw material and products including ethanol, pulp and acetic acid. Electricity is not assumed in this metric as the mass intensity is not valid for it. Table4.8 summarizes the mass balances of raw materials, ethanol and other co-products.

Table4.8. Balances for mass intensity metric

Pathways	Raw material (Kg/hr)	Output (Kg/hr)			total
		Ethanol	Pulp	Acetic acid	
GF: T/S	100000	22530	0	0	22530
GF: W/C	83333	26452	0	0	26452
RF: W/C	175000	26459	41667	0	68126
RF: VPP	99755	1646	41667	1879	45192

As the type and quality of process energy used can significantly affect the overall results of ethanol LCA, it should be considered as an environmental metric for evaluation of different scenarios. Energy efficiency is expressed as MJ per unit output. It is a measure of the net fuel-energy consumed to provide the heat and power requirements for the process. Energy inputs to the process include natural gas, gasoline and diesel. Steam or electricity that is exported from the process is credited in the metric by subtracting the exported energy in terms of fuel energy from the fuel energy consumed in the products including ethanol, pulp, electricity and acetic acid. Table4.9 shows the energy input and output of the different pathways.

Table4.9. Energy balances for energy efficiency metric

Energy input (MJ/hr)	**GF: T/S**	**GF: W/C**	**RF: W/C**	**RF: VPP**
Raw material	2.E+06	1.E+06	3.E+06	2.E+06
Pre-manufacturing	6.E+03	1.E+04	2.E+04	1.E+04
Mannufacturing	0.E+00	0.E+00	9.E+03	7.E+04
Energy output (MJ/hr)	**GF: T/S**	**GF: W/C**	**RF: W/C**	**RF: VPP**
Pulp	0.E+00	0.E+00	8.E+05	8.E+05
Acetic acid	0.E+00	0.E+00	0.E+00	3.E+04
Ethanol	7.E+05	8.E+05	8.E+05	5.E+04
Electricity	3.E+04	4.E+04	0.E+00	7.E+04
Energy flows (MJ/hr)	**GF: T/S**	**GF: W/C**	**RF: W/C**	**RF: VPP**
input	2.E+06	1.E+06	3.E+06	2.E+06
Output	7.E+05	8.E+05	2.E+06	9.E+05

According to this metric, the overall energy used for all products are brought into the account. As energy consumption is an important criterion in evaluation of each process, considering this metrics is also helpful for the comparison. This metric analyses the total amount of energy used for the whole process starting from the biomass cultivation to the gate of the mill considering ethanol and all other products. In this study, we try to find the amount of fossil fuel which is consumed for the production of ethanol. This is accessible by dividing the total energy consumptions and allocating it for ethanol and all the co-products produced in the process. As a result, this metric is calculated based on MJ fossil fuels needed for MJ of ethanol produced. For second generation of ethanol, the main parameters influencing fossil-fuel inputs are the fuel used by machinery to harvest and transport the biomass to the processing plant and the energy applied for chemicals used in the pre-fermentation process. In case of triticale straw-to-ethanol the production of nitrogen fertilizers also affects the results.

4.2.7. Methodology for interpretation of results

The final step of the methodology is the interpretation following the ISO guidelines. The objective of the interpretation phase is to evaluate the study in order to draw conclusion, explain limitations and give recommendations based on the inventory results. Generally, the type of conclusions depends on the intended application. In this study, in order to improve the opportunities for environmental performance for ethanol production, sensitivity and scenario analyses are used.

Some parameters such as electricity production at the mill can have a significant impact on the category indicator results. These parameters should be identified and considered when defining the mill configuration. Although, there is not a direct control over these parameters, their identification is useful in order to focus attention on the parameters that contribute most to the uncertainty of category indicator results.

4.2.7.1. Identification of key parameters

A large number of parameters are introduced in the life cycle inventory phase, depending on the scope and complexity of the study. It is important to select key parameters systematically. The selection of key parameters in this study was performed based on the approach proposed by Salzar et al. [76].

The procedure of key parameter selection is explained below, for the example of global warming (GW).

1. Calculation of the contribution per substances with the significant contribution to the results. The major GHGs include carbon dioxide (CO_2), methane (CH_4) nitrous oxide (N_2O), Fluorine (PFCs) and Chlorine (HPCs). Among these greenhouse gases, those with significant contribution should be selected. The total amount of these GHGs is illustrated in Table4.10.

Table4.10. Contribution of substances

Substance	Total (gr)	Contribution
Carbone dioxide	2650	93%
Methane	0.103	2%
Nitrous oxide	2.22	1%

For example 93% of the total GW indicator result is contributed by CO_2.

2. Calculation the contribution of unit processes on the total emission of each substance selected in the first step. The results of this step are summarized in Table4. 11.

Table4. 11. Unit process contributions to total CO_2 emission

Unit process	Contribution
Electricity production	33%
Transportation	19%
Fossil fuel	11%
Chemical production	7%

Fossil fuel is used for the generation of process steam in the pulp mill.

3. Calculation the contribution of each unit process/emission pair to the category results by multiplying the contribution calculated in steps 1 and 2. The results are illustrated in Table4.12.

Table4.12. Contribution of total unit process/emission pairs on the total GW potential

Unit process	Emission	Contribution
Electricity production	CO_2	30%
Transportation	CO_2	17%
Fossil fuel	CO_2	10%
Chemical production	CO_2	2%

4. Selection the key parameters with the contribution of more than 10%.

With this methodology the selected key parameters are illustrated in the following table. These key parameters include electricity production, transportation (radius of collecting biomass) and energy source used in the process.

Table4.13. Selected key parameters for sensitivity and scenario analyses

Unit process	Unit
Electricity production	KWh/MJ EToH
Transportation	tkm/ MJ EToH
Fossil fuel	MJ/MJ EToH

4.2.7.1.1. Key parameters for scenario analyses

Two parameters including electricity production and energy source are selected for scenario analyses.

In the baseline model, VPP, the electricity is provided by the average Canadian grid mix and the steam needed for the process is produced by natural gas. For the scenario analyses two other electricity-oriented alternatives including North American and Quebec's grid mix and three other energy-oriented alternatives including using oil, coil and pellet for steam production are assumed. These selections are summarized in Table4.14 .

Table4.14. Different scenario analyses and their parameters

Scenario analysis	Parameters	GF: T/S	GF: W/C	RF: W/C	RF: VPP
Analysis #1 (Electricity production in different regions)	Ave. Canadian (Baseline)	✓	✓	✓	✓
	North America				
	Quebec				
Analysis # 2 (Source of energy used in the process)	Natural gas (Baseline)			✓	✓
	Oil				
	Coal				
	Pellet				

As mentioned in the table, the corresponding power mixes used for scenario analysis include North American (NA), Quebec province (QC) and average Canadian (Ave. CAN) as the base line model. The differences of these scenarios are shown in Table4.15.

Table4.15. Power mixes for three regions

Scenarios for electricity grid mix	Hydro (%)	Fossil (%)	Nuclear (%)
North america	14	67	19
Aveage Canadian	57	27	15
Quebec	95	0	3

Transportation key parameter is assumed for sensitivity analysis. In the baseline model the radius of collecting biomass is assumed 200 Km.

4.2.7.1.2. Key parameters for sensitivity analyses

In the baseline model, the radius collection for feedstock needed for ethanol production is assumed to be 200 Km. In order to assess the effects of the biomass collection distance in the results, different alternatives including 150, 300 and 500 Km were defined. These assumptions are illustrated in Table4.16.

Table4.16. Sensitivity parameters regarding to radius of biomass collection

Sensitivity parameter	Minimum	Maximum	Unit
Distance of biomass collection	150	500	Km

Another important key parameter for an LCA study, based on ISO standard is allocation procedures. This parameter is also assumed in this study for sensitivity analysis. It is explained in details in the following section.

4.2.7.2. Assessment of uncertainties due to allocation procedures

According to ISO standard, for processes with outputs environmental burdens should be allocated [28]. This is another objective of the interpretation phase for assessment the uncertainties due to allocation rules. In this study, environmental burdens are allocated not only to ethanol, but also to other co-products based on the energy content and economic relationship. The effects of this approach was assessed in the baseline model and later applied to the different scenarios for ethanol production in order to compare their consequent results over the baseline model.

4.2.7.2.1. Physical allocation

Selection of the environmental burdens allocated for ethanol in physical approach is based on the energy contents of the products and co-products including ethanol, pulp, acetic acid and electricity. The contribution of environmental impacts for each product for physical allocation is presented in Table4.17.

Table4.17. Selection of environmental burdens due to physical allocation

Products	Contribution of environmental burdens			
	GF: T/S	GF: W/C	RF: W/C	RF: VPP
Ethanol	96%	95%	49%	5%
Electricity	4%	5%	N/A	7%
Pulp	N/A	N/A	51%	85%
Acetic acid	N/A	N/A	N/A	3%

4.7.2.2.2. Economic allocation

Selection of the environmental burdens allocated for ethanol and co-products in economic approach is calculated based on the market price of each product. The selected price and the contribution of environmental impacts based on that are presented in Table4.18.

Table4.18. Selection of environmental burdens due to economic allocation

Products	Unit	Price		Contribution of environmental burdens			
		Min.	Max.	GF:T/S	GF:W/C	RF: W/C	RF: VPP
Ethanol	$/Gallon	1.6	2.05	82%	80%	30%	2%
Electricity	$/KWh	5.8	6.7	18%	20%	N/A	14%
Pulp	$/adt	554	648	N/A	N/A	70%	75%
Acetic acid	$/lb	0.67	0.69	N/A	N/A	N/A	9%

Next step is the application of the methodology, first in the baseline model and then in all ethanol scenarios. The results of this application is explained in chapter 5 following by discussion.

Chapter 5- Results and discussion

5.1. Impacts assessment results

As explained before, the VPP process was selected as the baseline model. The functional unit of this LCA study is defined based on the VPP process and system expansion procedure is used in order to avoid allocation. The methodological choices used in this thesis for comparison of different ethanol pathways are summarized in the Table 5. 1

Table 5. 1. Selected methodological choices

Methodology	Selected method
Goal	To compare the environmental performance of ethanol production from different feedstocks
System boundaries	Cradle-to-gate
Functional unit	1 MJ ethanol + 0.06177 MJ electricity + 4.229e-5 T acetic acid + 0.000937 T pulp
Allocation approach	Avoiding allocation/ System expansion
Environmental impact indicators	Human toxicity, respiratory effects, ionizing radiation, ozone layer depletion, photochemical oxidation, aquatic ecotoxicity, terrestrial ecotoxicity, terrestrial acidification/nutrification, aquatic acidification, aquatic eutrophication, land occupation, global warming, non-renewable energy, mineral extraction
LCIA method	Impact 2002 $^{+}$

According to the methodology applied to the VPP process, the impact assessment results are presented in Table 5.2.

Table 5.2. Category indicator results

Impact category	Unit	Total
Carcinogens	kg C2H3Cl eq	4.67E-03
Non-carcinogens	kg C2H3Cl eq	9.02E-03
Respiratory inorganics	kg PM2.5 eq	5.81E-04
Ionizing radiation	Bq C-14 eq	1.03E+01
Ozone layer depletion	kg CFC-11 eq	4.81E-08
Respiratory organics	kg C2H4 eq	2.70E-04
Aquatic ecotoxicity	kg TEG water	4.31E+01
Terrestrial ecotoxicity	kg TEG soil	9.49E+00
Terrestrial acid/nutri	kg SO2 eq	1.47E-02
Land occupation	m2org.arable	9.47E-02
Aquatic acidification	kg SO2 eq	3.97E-03
Aquatic eutrophication	kg PO4 P-lim	3.83E-05
Global warming	kg CO2 eq	5.19E-01
Non-renewable energy	MJ primary	9.02E+00
Mineral extraction	MJ surplus	9.53E-03

5.2. Interpretation of results

5.2.1. Sensitivity analysis

According to methodology for selection of sensitivity parameters presented before, allocation procedure and radius of biomass collection were chosen in order to assess their consequences in the LCA results. The results for these parameters are presented in the following.

5.2.1.1. Allocation

Table 5.3 shows the characterization results for the production of 1 MJ ethanol using two alternative approaches for by-product allocation in the VPP process. In general, the alternative approaches do not significantly change the characterization results. When environmental burdens are allocated to ethanol based on physical and economic relationship, the results vary from 2 to 5% with respect to baseline model (system expansion).

Table 5.3. Characterization results for alternative allocation approaches in the VPP ethanol production

Impact category	Unit	Alternative 1 (Physical allocation)	Alternative 2 (Economic allocation)
Carcinogens	kg C2H3Cl eq	2.33E-04	1.09E-04
Non-carcinogens	kg C2H3Cl eq	4.51E-04	2.10E-04
Respiratory inorganics	kg PM2.5 eq	2.90E-05	1.35E-05
Ionizing radiation	Bq C-14 eq	5.14E-01	2.39E-01
Ozone layer depletion	kg CFC-11 eq	2.41E-09	1.12E-09
Respiratory organics	kg C2H4 eq	1.35E-05	6.28E-06
Aquatic ecotoxicity	kg TEG water	2.16E+00	1.00E+00
Terrestrial ecotoxicity	kg TEG soil	4.74E-01	2.21E-01
Terrestrial acid/nutri	kg SO2 eq	7.34E-04	3.42E-04
Land occupation	m2org.arable	4.74E-03	2.21E-03
Aquatic acidification	kg SO2 eq	1.98E-04	9.24E-05
Aquatic eutrophication	kg PO4 P-lim	1.91E-06	8.92E-07
Global warming	kg CO2 eq	2.60E-02	1.21E-02
Non-renewable energy	MJ primary	4.51E-01	2.10E-01
Mineral extraction	MJ surplus	4.76E-04	2.22E-04

5.2.1.2. Radius of biomass collection

Table 5.4 presents the sensitivity analysis results for the selected radius of biomass collection parameters. The alternatives assumed for this analysis are 150, 200, 300 and 500 Km.

Table 5.4. Characterization results for radius of biomass collection in the VPP ethanol production

Impact category	Unit	150 Km	200 Km (Baseline)	300 Km	500 Km
Carcinogens	kg C2H3Cl eq	4.43E-03	4.67E-03	5.10E-03	5.99E-03
Non-carcinogens	kg C2H3Cl eq	8.65E-03	9.02E-03	9.72E-03	1.11E-02
Respiratory inorganics	kg PM2.5 eq	5.28E-04	5.81E-04	6.77E-04	8.77E-04
Ionizing radiation	Bq C-14 eq	1.01E+01	1.03E+01	1.05E+01	1.11E+01
Ozone layer depletion	kg CFC-11 eq	4.25E-08	4.81E-08	5.84E-08	7.95E-08
Respiratory organics	kg C2H4 eq	2.39E-04	2.70E-04	3.25E-04	4.41E-04
Aquatic ecotoxicity	kg TEG water	4.11E+01	4.31E+01	4.68E+01	5.44E+01
Terrestrial ecotoxicity	kg TEG soil	8.18E+00	9.49E+00	1.19E+01	1.68E+01
Terrestrial acid/nutri	kg SO2 eq	1.30E-02	1.47E-02	1.77E-02	2.41E-02
Land occupation	m2org.arable	9.44E-02	9.47E-02	9.53E-02	9.63E-02
Aquatic acidification	kg SO2 eq	3.72E-03	3.97E-03	4.42E-03	5.35E-03
Aquatic eutrophication	kg PO4 P-lim	3.62E-05	3.83E-05	4.21E-05	4.99E-05
Global warming	kg CO2 eq	4.84E-01	5.19E-01	5.84E-01	7.18E-01
Non-renewable energy	MJ primary	8.43E+00	9.02E+00	1.01E+01	1.23E+01
Mineral extraction	MJ surplus	9.25E-03	9.53E-03	1.00E-02	1.11E-02

As the effect of this parameter contributes differently to the different impact categories, Kg of CO_2 equivalent are considered to illustrate this sensitivity analysis. The percentages of this alternative changed based on different assumptions for radius of biomass collection is shown in Figure 5.1.

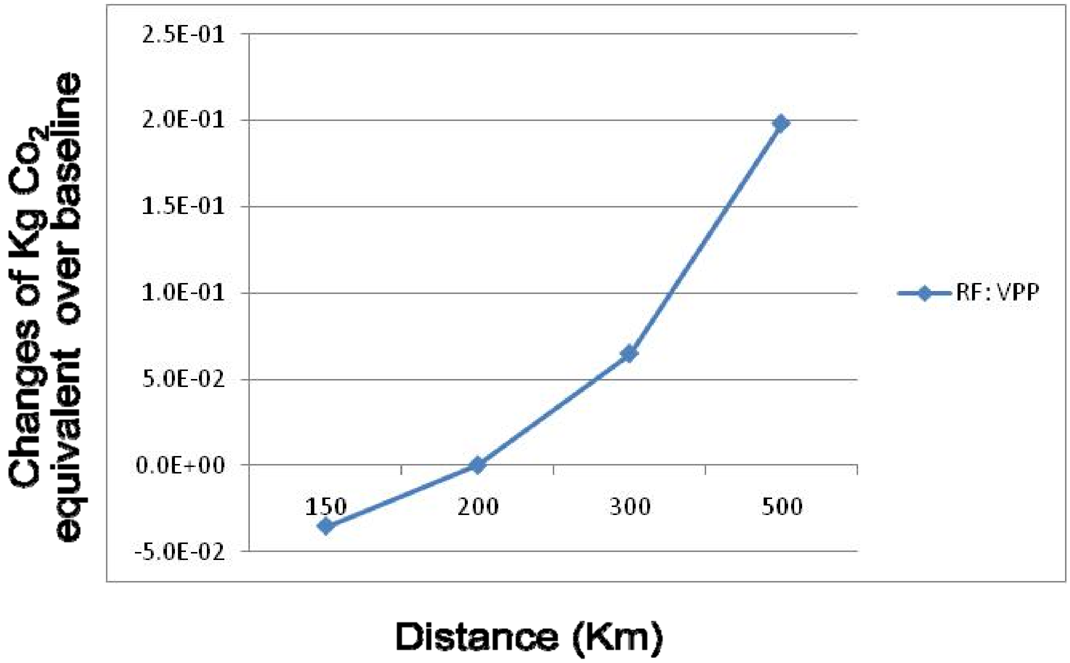

Figure 5.1. Changes for Kg of CO2 equivalent based on the different radius of biomass collection

According to the graph, it is observed that the amount of emission of CO_2 is not highly sensitive to the radius of biomass collection. For example, the amount of CO_2 is changed 0.065 Kg if the radios of biomass collection is increased from 200 to 300 Km. This amount is more sensitive when increasing the distance to 500 Km.

5.2.2. Scenario analysis

As mentioned before, the key parameters for scenario analyses include the electricity production (Electricity-oriented scenario) and fossil fuels (Energy-oriented scenario) used in the process. These scenarios are explained below.

5.2.2.1. Electricity-oriented scenario

Considering the VPP process as the baseline, there is not any electricity input to the process. Consequently LCA results are not changed by using different alternatives for the electricity-oriented scenario. But it is essential when comparing different models in this study as electricity production has significant effect on the result.

5.2.2.2. Energy-oriented scenario

Table 5.5 presents the characterization results for the source of energy and Table 5.6 shows the normalized profile for different alternative energy-scenarios. The normalization reference is the baseline model, VPP by using natural gas as the fossil fuel source in the process.

Table 5.5.Characterization results for the source of energy used in the process through the VPP ethanol production

Impact category	Unit	Source of energy used in the process			
		Natural gas	Oil	Coal	Pellet
Carcinogens	kg C2H3Cl eq	4.67E-03	4.63E-03	4.63E-03	4.63E-03
Non-carcinogens	kg C2H3Cl eq	9.02E-03	9.04E-03	9.15E-03	9.13E-03
Respiratory inorganics	kg PM2.5 eq	5.81E-04	5.82E-04	5.87E-04	5.83E-04
Ionizing radiation	Bq C-14 eq	1.03E+01	1.03E+01	1.03E+01	1.03E+01
Ozone layer depletion	kg CFC-11 eq	4.81E-08	4.82E-08	4.73E-08	4.74E-08
Respiratory organics	kg C2H4 eq	2.70E-04	2.70E-04	2.69E-04	2.69E-04
Aquatic ecotoxicity	kg TEG water	4.31E+01	4.33E+01	4.37E+01	4.38E+01
Terrestrial ecotoxicity	kg TEG soil	9.49E+00	9.52E+00	9.62E+00	9.74E+00
Terrestrial acid/nutri	kg SO2 eq	1.47E-02	1.47E-02	1.48E-02	1.47E-02
Land occupation	m2org.arable	9.47E-02	9.47E-02	9.47E-02	9.49E-02
Aquatic acidification	kg SO2 eq	3.97E-03	3.98E-03	4.02E-03	3.97E-03
Aquatic eutrophication	kg PO4 P-lim	3.83E-05	3.87E-05	3.83E-05	3.86E-05
Global warming	kg CO2 eq	5.19E-01	5.21E-01	5.22E-01	5.16E-01
Non-renewable energy	MJ primary	9.02E+00	9.02E+00	9.00E+00	8.94E+00
Mineral extraction	MJ surplus	9.53E-03	9.54E-03	9.52E-03	9.53E-03

According to the normalized results in table Table 5.6, it is observed that impacts assessment was mostly focused on terrestrial ecotoxicity, global warming and non-renewable energy results. It should be noted that values lower than 1 represent a decrease in the potential impact and therefore, an increase in the environmental performance. Terrestrial ecotoxicity category is sensitive to the impact of toxic substances such as Zinc and Aluminum into the soil ecosystem. As a result, using pellet as the energy source increases this impact category results because of the raw material cultivation included in the life cycle of pellet production. On the other hand, using pellet reduces the amount of CO_2 emissions to the atmosphere and the consumption of non-renewable energy.

Table 5.6.Normalized profile for alternative energy-oriented scenarios (Normalization reference: baseline model)

Impact category	Source of energy used in the process		
	Oil	Coal	Pellet
Carcinogens	0.99	0.99	0.99
Non-carcinogens	1.00	1.01	1.01
Respiratory inorganics	1.00	1.01	1.00
Ionizing radiation	1.00	1.00	1.00
Ozone layer depletion	1.00	0.98	0.98
Respiratory organics	1.00	1.00	1.00
Aquatic ecotoxicity	1.00	1.01	1.02
Terrestrial ecotoxicity	1.00	1.01	1.03
Terrestrial acid/nutri	1.00	1.01	1.00
Land occupation	1.00	1.00	1.00
Aquatic acidification	1.00	1.01	1.00
Aquatic eutrophication	1.01	1.00	1.01
Global warming	1.00	1.00	0.99
Non-renewable energy	1.00	1.00	0.99
Mineral extraction	1.00	1.00	1.00

5.3. Comparison of different ethanol pathways

As mentioned before, four ethanol scenarios defined for this study include the ethanol production from triticale straw, woodchips in greenfield and retrofit pathways and hemicelluloses in the VPP process. In the previous section, the methodology was applied to the VPP process as the base case scenario. In this section, the LCA-based methodology was applied to all scenarios. The comparative results are presented in two groups including LCA-based and study specific-based metrics. The results of sensitivity and scenario analyses for all pathways are also presented in this section. Table 5.7 shows the terms used for different pathways in this study.

Table 5.7. Terms used in this study for different ethanol pathways

Feedstock	Terms used in this study
Greenfield, Triticale straw	GF: T/S
Greenfield, Woodchips	GF: W/C
Retrofit, Woodchips	RF: W/C
Retrofit, Hemicellulose (Value Prior Pulping)	RF: VPP

5.3.1. LCA-based metrics

Table 5.8 shows the characterized LCA results for all scenarios of ethanol conversion. These impact categories are chosen according to the methodology for the selection of environmental evaluation metrics proposed in section 4.2.6.1. The total results for all impact categories are presented in Table C.1 in appendix C.

Table 5.8. Characterized LCA results for all scenarios

Impact category	Unit	GF:T/S	GF: W/C	RF: W/C	RF: VPP
Respiratory inorganics	kg PM2.5 eq	5.18E-04	4.82E-04	4.83E-04	5.81E-04
Terrestrial ecotoxicity	kg TEG soil	1.56E+01	8.94E+00	8.95E+00	9.49E+00
Land occupation	m2org.arable	8.95E-02	9.22E-02	9.22E-02	9.47E-02
Global warming	kg CO2 eq	5.07E-01	4.78E-01	4.79E-01	5.19E-01
Non-renewable energy	MJ primary	9.45E+00	9.09E+00	9.10E+00	9.02E+00

In order to identify the most environmental friendly pathway, the characterization results are normalized based on the VPP process as the reference model. Table 5.9 shows the normalized profile for different pathways. It should be noted that values lower than 1 in this table represent a decrease in the potential impact and therefore, an increase in the environmental performance.

Table 5.9. Normalized profile for different pathways based on reference model (VPP)

Impact category	GF:T/S	GF: W/C	RF: W/C
Respiratory inorganics	8.92E-01	8.30E-01	8.31E-01
Terrestrial ecotoxicity	1.64E+00	9.43E-01	9.43E-01
Land occupation	9.44E-01	9.73E-01	9.74E-01
Global warming	9.76E-01	9.21E-01	9.21E-01
Non-renewable energy	1.05E+00	1.01E+00	1.01E+00

According to the normalized results, all the ethanol pathways have a better environmental performance compared to the VPP process based on the most impact categories. The only significant difference is for ethanol production from triticale straw according to the terrestrial ecotoxicity category. In this specific impact category, triticale straw-based ethanol is less environmentally friendly than the VPP process. It is resulted because of metals like Zinc, Chromium and Aluminum emitted into soil during pre-manufacturing of triticale straw such as baling.

5.3.1.1. Sensitivity analysis

As defined before, two sensitivity analyses including the selection of allocation parameters and the radius of biomass collection were selected. In this section they were applied to all scenarios. Table 5.10 and Table 5.11 present the characterization results of allocation alternatives and radius of biomass collection respectively based on the selected LCA-based metrics for the production of 1 MJ ethanol through different pathways. The total results for all impact categories are presented in Table C.2 and Table C.3 for all scenarios in appendix C.

According to Table 5.10, when environmental burdens are allocated to ethanol and by-products based on the physical and economic relationship; a significant change does not occur between these two alternatives. As an example, the contribution of environmental burdens allocated to ethanol in greenfield pathway using woodchips as feedstocks (GF:W/C) is 95% in physical allocation although this amount is assumed 80% based on the market price when using economic allocation. Consequently, the environmental impacts of these two allocations for 1 MJ of ethanol do not make a big difference.

By comparing the results when using allocation procedures and avoiding allocation, it is obvious that the environmental impacts associated with ethanol production done by the system expansion are the highest. Sensitivity analyses show that the allocation approach chosen influences the results more than any other parameter investigated. The difference in the environmental impact results varies up to 40% between the various allocation approaches. This occurs because of the net energy of the different ethanol scenarios and the yield of ethanol produced. However, the same trend occurs when using all of the allocation procedures for the various ethanol scenarios which can be used to select the preferred environmental scenarios.

With respect to the radios of biomass collection, results show that retrofit pathways are more sensitive to the radius of biomass collection compared to the greenfiled pathways. But in general, it is obvious that LCA results are not highly sensitive to this parameter.

Table 5.10. Characterization results of allocation alternatives based on the selected LA-based metrics for different pathways

Impact category	Unit	System expansion (Baseline model)				Physical allocation				Economic allocation			
		GF:T/S	GF: W/C	RF: W/C	RF: VPP	GF:T/S	GF: W/C	RF: W/C	RF: VPP	GF:T/S	GF: W/C	RF: W/C	RF: VPP
Respiratory inorganics	kg PM2.5 eq	5.18E-04	4.82E-04	4.83E-04	5.81E-04	5.47E-05	1.77E-05	9.15E-06	2.90E-05	4.73E-05	1.53E-05	6.35E-06	1.35E-05
Terrestrial ecotoxicity	kg TEG soil	1.56E+01	8.94E+00	8.95E+00	9.49E+00	6.73E+00	3.11E-01	1.60E-01	4.74E-01	5.82E+00	2.68E-01	1.11E-01	2.21E-01
Land occupation	m2org.arable	8.95E-02	9.22E-02	9.22E-02	9.47E-02	2.30E-03	4.87E-03	2.51E-03	4.74E-03	1.99E-03	4.21E-03	1.74E-03	2.21E-03
Global warming	kg CO2 eq	5.07E-01	4.78E-01	4.79E-01	5.19E-01	4.42E-02	1.27E-02	6.57E-03	2.60E-02	3.82E-02	1.10E-02	4.56E-03	1.21E-02
Non-renewable energy	MJ primary	9.45E+00	9.09E+00	9.10E+00	9.02E+00	6.80E-01	2.15E-01	1.11E-01	4.51E-01	5.88E-01	1.85E-01	7.69E-02	2.10E-01

Table 5.11. Characterization results of radius of biomass collection alternatives based on the selected LA-based metrics for different pathways

Impact category	Unit	150 Km				200 Km				300 Km				500 Km			
		GF:T/S	GF: W/C	RF: W/C	RF: VPP	GF:T/S	GF: W/C	RF: W/C	RF: VPP	GF:T/S	GF: W/C	RF: W/C	RF: VPP	GF:T/S	GF: W/C	RF: W/C	RF: VPP
Respiratory inorganics	kg PM2.5 eq	5.15E-04	4.79E-04	4.34E-04	5.28E-04	5.18E-04	4.82E-04	4.83E-04	5.81E-04	5.24E-04	4.87E-04	5.79E-04	6.77E-04	5.36E-04	4.98E-04	7.73E-04	8.77E-04
Terrestrial ecotoxicity	kg TEG soil	1.55E+01	8.88E+00	7.75E+00	8.18E+00	1.56E+01	8.94E+00	8.95E+00	9.49E+00	1.57E+01	9.07E+00	1.13E+01	1.19E+01	1.60E+01	9.33E+00	1.61E+01	1.68E+01
Land occupation	m2org.arable	1.28E-01	9.22E-02	9.20E-02	9.44E-02	1.28E-01	9.22E-02	9.22E-02	9.47E-02	1.28E-01	9.22E-02	9.28E-02	9.53E-02	1.28E-01	9.23E-02	9.38E-02	9.63E-02
Global warming	kg CO2 eq	5.05E-01	4.76E-01	4.46E-01	4.84E-01	5.07E-01	4.78E-01	4.79E-01	5.19E-01	5.11E-01	4.82E-01	5.43E-01	5.84E-01	5.19E-01	4.89E-01	6.73E-01	7.18E-01
Non-renewable energy	MJ primary	9.41E+00	9.06E+00	8.56E+00	8.43E+00	9.45E+00	9.09E+00	9.10E+00	9.02E+00	9.51E+00	9.15E+00	1.02E+01	1.01E+01	9.65E+00	9.26E+00	1.23E+01	1.23E+01

5.3.1.2. Scenario analysis

a. Electricity-orientated scenario

The characterization inventory results per 1 MJ of ethanol are presented for different ethanol pathways in Table 5.12.

In order to have a better understanding of the comparison different ethanol production pathways, characterization results are normalized based on the VPP baseline model (using average Canadian grid mix), these results are presented in Table 5.13. The total results for all impact categories are presented Table C.4 **Erreur ! Source du renvoi introuvable.** in appendix C.

It should be noted that values lower than 1 represent a decrease in the potential impact and, therefore, an increase in the environmental performance of ethanol production.

In general, most of impact categories for different ethanol production scenarios with respect to electricity consumption present values less than 1. But there are some values which present the less environmental performance of ethanol production compared to the VPP model.

For example, with respect to the global warming and non-renewable energy impact categories, results for triticale straw are more than 1 when using the North American electricity grid mix. This results show that locating triticale-to-ethanol production mill in North America, make this scenario less environmental friendly compared to the VPP process by using average the Canadian, North American or Quebec's electricity grid mix.

According to the results considering an attribution LCA study, this scenario defines the best environmental alternatives for the management of the location for ethanol production.

Table 5.12. Inventory results for alternative electricity-oriented scenario

Impact category	Unit	Average Canadian				North America				Quebec			
		GF:T/S	GF: W/C	RF: W/C	RF: VPP	GF:T/S	GF: W/C	RF: W/C	RF: VPP	GF:T/S	GF: W/C	RF: W/C	RF: VPP
Respiratory inorganics	kg PM2.5 eq	5.18E-04	4.82E-04	4.83E-04	5.81E-04	5.30E-04	4.94E-04	4.95E-04	5.81E-04	5.07E-04	4.71E-04	4.71E-04	5.81E-04
Terrestrial ecotoxicity	kg TEG soil	1.56E+01	8.94E+00	8.95E+00	9.49E+00	1.57E+01	9.03E+00	9.04E+00	9.49E+00	1.55E+01	8.89E+00	8.89E+00	9.49E+00
Land occupation	m2org.arable	8.95E-02	9.22E-02	9.22E-02	9.47E-02	8.96E-02	9.23E-02	9.23E-02	9.47E-02	8.94E-02	9.22E-02	9.22E-02	9.47E-02
Global warming	kg CO2 eq	5.07E-01	4.78E-01	4.79E-01	5.19E-01	5.29E-01	5.00E-01	5.01E-01	5.19E-01	4.92E-01	4.63E-01	4.63E-01	5.19E-01
Non-renewable energy	MJ primary	9.45E+00	9.09E+00	9.10E+00	9.02E+00	9.78E+00	9.42E+00	9.45E+00	9.02E+00	9.15E+00	8.79E+00	8.79E+00	9.02E+00

Table 5.13. Normalized profile for alternative electricity-oriented scenarios (Normalization reference: Baseline model)

Impact category	Average Canadian			North America			Quebec		
	GF:T/S	GF: W/C	RF: W/C	GF:T/S	GF: W/C	RF: W/C	GF:T/S	GF: W/C	RF: W/C
Respiratory inorganics	8.92E-01	8.30E-01	8.31E-01	9.13E-01	8.51E-01	8.53E-01	8.73E-01	8.11E-01	8.12E-01
Terrestrial ecotoxicity	1.64E+00	9.43E-01	9.43E-01	1.65E+00	9.52E-01	9.53E-01	1.64E+00	9.37E-01	9.37E-01
Land occupation	9.44E-01	9.73E-01	9.74E-01	9.45E-01	9.75E-01	9.75E-01	9.44E-01	9.73E-01	9.73E-01
Global warming	9.76E-01	9.21E-01	9.21E-01	1.02E+00	9.63E-01	9.65E-01	9.47E-01	8.91E-01	8.91E-01
Non-renewable energy	1.05E+00	1.01E+00	1.01E+00	1.08E+00	1.05E+00	1.05E+00	1.02E+00	9.75E-01	9.75E-01

b. Energy-orientated scenario

Since the source of heat process represents a significant contribution to most of the impact categories, the effect of changing the heat production model using different sources is assessed. As explained before, the two greenfield pathways including triticale straw and woodchips are self- energy sufficient. As a result, this scenario is not applicable for the greenfield pathways.

The characterization inventory results per 1 MJ of ethanol for retrofit woodchips-to-ethanol and the VPP process are presented in Table 5.14. Table 5.15 shows the normalized results of two pathways when using different energy sources based on the VPP baseline model. The total results for all impact categories are presented Table C.5 in appendix C.

The normalized profiles for alternative the energy-oriented scenario show that ethanol production is not high sensitive to the source of energy when using oil or coal instead of natural gas. But when the process heat of the retrofit pathways are provided by using pellet instead of natural gas, the amount of CO_2 emitted to the environment is decreased but on the other hand, the terrestrial ecotoxicity impact results are increased in the system.

Table 5.14. Inventory results for alternative energy-oriented scenario

Impact category	Unit	Natural gas		Oil		Coal		Pellet	
		RF: W/C	RF: VPP	RF: W/C	RF: VPP	RF: W/C	RF: VPP	RF: W/C	RF: VPP
Respiratory inorganics	kg PM2.5 eq	4.83E-04	5.81E-04	4.84E-04	5.82E-04	4.88E-04	5.87E-04	4.85E-04	5.83E-04
Terrestrial ecotoxicity	kg TEG soil	8.95E+00	9.49E+00	8.98E+00	9.52E+00	9.07E+00	9.62E+00	9.19E+00	9.74E+00
Land occupation	m2org.arable	9.22E-02	9.47E-02	9.22E-02	9.47E-02	9.23E-02	9.47E-02	9.24E-02	9.49E-02
Global warming	kg CO2 eq	4.79E-01	5.19E-01	4.80E-01	5.21E-01	4.81E-01	5.22E-01	4.75E-01	5.16E-01
Non-renewable energy	MJ primary	9.10E+00	9.02E+00	9.10E+00	9.02E+00	9.08E+00	9.00E+00	9.03E+00	8.94E+00

Table 5.15. Normalized profile for alternative energy-oriented scenarios (Normalization reference: Baseline model)

Impact category	Oil		Coal		Pellet	
	RF: W/C	RF: VPP	RF: W/C	RF: VPP	RF: W/C	RF: VPP
Respiratory inorganics	1.00E+00	1.00E+00	1.01E+00	1.01E+00	1.00E+00	1.00E+00
Terrestrial ecotoxicity	1.00E+00	1.00E+00	1.01E+00	1.01E+00	1.03E+00	1.03E+00
Land occupation	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00
Global warming	1.00E+00	1.00E+00	1.00E+00	1.00E+00	9.93E-01	9.93E-01
Non-renewable energy	1.00E+00	1.00E+00	9.98E-01	9.98E-01	9.92E-01	9.92E-01

5.3.2. Other metrics

As explained before, mass intensity, energy efficiency and MJ of fossil fuel allocated for production of 1 MJ of ethanol are three metrics which are selected based on the goal and scope of this study. Table 5.16 shows the results of these metrics for all scenarios.

Table 5.16. Other environmental metrics for all scenarios

Metrics	GF: T/S	GF: W/C	RF: W/C	RF: VPP
Mass intensity (%)	23	32	39	45
Energy Efficiency (%)	41	58	53	53
MJ of fossil fuels/MJ of ETOH	7.0E-04	4.8E-04	1.5E-02	1.8E+00

According to the results, VPP is the best alternative based on the mass intensity metric. With respect to energy efficiency, greenfield and retrofit woodchips-to-ethanol and the VPP pathways have the most environmental friendly performances respectively. The consumption of a small amount of fossil fuels in pre-manufacturing step makes these scenarios environmentally preferable.

These two metrics make the VPP process an interesting choice for ethanol production; however it consumes the highest MJ of fossil fuels for production of 1 MJ of ethanol. This metric change the results for selection of VPP as the best alternative.

Greenfield pathways including triticale straw and woodchips are the best options based on the MJ of fossil fuels/MJ of ethanol metric.

Due to the very small amount of fossil fuel used in the pre-manufacturing step of the mentioned models. In retrofit ethanol scenario (RF: W/C) and the VPP scenario (RF:VPP), fossil fuels are used in the pre-manufacturing and the process lines. This makes them less of an environmental preferable scenario as compared to the greenfield scenarios.

Chapter 6- Conclusion, contribution and recommendation

6.1. Conclusion

Studying the environmental performance of ethanol production is a complicated task as it evolves covering many different feedstock systems, conversion technologies as well as aspects related to the substituted products, including fossil transport fuels and electricity. As assessed in this research, LCA studies attribute a wide range of diverting results. This partly reflects the complexity and technological scope of the modeled reality. However, it is mainly because of the many different assumptions required to perform an LCA analysis. It is obvious that there are trade-offs for selection the most appropriate methodology for an ethanol LCA. This compromise poses a challenge for LCA analyzer with regards to selecting different methodological choices based on the specific case for ethanol production.

This research project has introduced a systematic approach to the application of LCA in the ethanol production from different feedstocks. An LCA-based methodology was developed to sequence the methodological choices such as system boundary, environmental impact category and the allocation procedure by reviewing 26 LCA studies for ethanol production. The methodological choices for this research project include cradle-to-gate for system boundary, midpoint impact for the environmental impact categories and system expansion in order to avoid the allocation procedure in the models. Among these selections, allocation procedure is the one of the most uncertainty in each LCA. During the application of the LCA-based methodology for all ethanol pathways, sensitivity analyses show that the allocation approach selected influences the inventory results more than other parameters and methodological choices. The difference between results obtained by avoiding allocation (system expansion) and allocation based on physical and economic relationship indicates that environmental impacts associated with ethanol production through system expansion are highest. The final results are most sensitive to 1) the production of pulp, and 2) the yield of the ethanol process.

Moreover, the additional benefit of proposed methodology in this research is the systematically selection of LCA-based and other environmental metrics for ethanol production. There is a clear need to reach harmony on how to carry out LCAs on ethanol production. This involves reaching agreement on approaches and assumptions on a wide set of key parameters. Indicators used for the comparison of different ethanol pathways can influence the result of the environmental evaluation strongly. Consequently, the set of metrics addresses the best environmental performance of ethanol production when comparing different pathways guaranties the decision making.

6.2. Contribution

The following are the main contributions to the body of knowledge from this research project, related with the initial stated main hypothesis and sub-hypotheses:

- A proposal of practical and systematic procedure for the evaluation of the ethanol production from different feedstocks and pathways in LCA-oriented framework towards the identification of opportunities to improve their environmental performance.
- Development of a rational set of metrics that describes the environmental performance of different ethanol biorefineries.
- Systematic comparison of ethanol production scenarios based on interpretative environmental metrics.

6.3. Future work

The following are recommended topics to be investigated in the future:

- Assessment of system integration into multi-fuel and multi-products Biorefinery
- Partial or complete substitution of the fossil-based feedstock with a biomass in the existing fossil-based process
- Incorporation of the ethanol biorefinery in a life cycle assessment with economic and social aspects for mitigation
- Combination of LCA with other environmental assessment tools looking at local and regional impacts in ethanol production.

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Appendix A: Comparative life-cycle assessments for different feedstocks-to-ethanol production

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ABSTRACT

Ethanol can be produced from different renewable resources or a combination of them. These different feedstocks play an important role because the source of biomass has a big impact on environmental evaluation. Life Cycle Assessment (LCA) is a methodology able to reveal the environmental performance of ethanol production. In this study, the LCA-based methodology is applied in order to have an environmental friendly decision for ethanol produced from different feedstocks.

Key words: Life Cycle Assessment, LCA, ethanol, Biorefinery, Integrated Forest Biorefinery (IFBR)

Introduction

Recently, climate change and environmental issues have increased the priority to find renewable sources for the production of transportation fuels. The environmental performance of the use of ethanol differs depending on the type of feedstock sources and pathways used for its production. This performance can be measured using Life Cycle Assessment (LCA) of the different ethanol production pathways. LCA is a tool to assess the potential environmental impacts and resources used throughout the ethanol life cycle from raw material to end use and waste management. It has four steps including goal and scope definition, Life Cycle Inventory analysis (LCI), Life Cycle Impact Assessment (LCIA) and interpretation [1]. The goal and scope definition determines the reasons for carrying out the study. In LCI step, all inputs and outputs from the product over its life-cycle are determined. The LCIA is aimed at understanding and evaluating the environmental impacts of the system. Finally, the results are evaluated in relation to the goal and scope in the interpretation step. Generally, two different LCA approaches, attributional

LCA (ALCA) and consequential LCA (CLCA), were identified and described [2-4]. ALCA describes the pollution and resource flows within a chosen system attributed to the delivery of a specified amount of the functional unit. CLCA estimates how pollution and resource flows within a system changes in response to a change in the output of the functional unit[5].

In this context, LCA can provide environmental performance information to support decision-making in the design process. Multi-criteria decision-making (MCDM) tool can consider the necessity of a broad range of environmental, economic and social deliberations in order to have a better decision for sustainability. In MCDM, the problem is structured and indicators are identified and characterized. The results are normalized and the importance of the attributes is evaluated based on weighting. Finally, alternatives are compared and sensitivity analyses are performed in order to identify the alternative that represents the best compromise between the different objectives.

Literature review

Ethanol can be produced from any source containing sugars and starch, currently the focus is also on ethanol production from lignocellulosic materials. Several articles with life-cycle orientation have already been published regarding the environmental performance of different biomass-to-ethanol production scenarios. In this study the focus is the second generation ethanol because of the conflict between food-based biomass and ethanol fuel in the first generation of ethanol production [5, 6]. Generally, non-food-based biomass includes residues, energy crops and waste. The waste and residues come from agricultural and forestry industries, and also households. Several publications are available on LCA studies carried out to identify the environmental performance of the production of ethanol from this group including baggasse, wheat straw, corn stover, municipal solid waste (MSW) and wood residues [2, 7-14]. These cellulosic raw materials are not specifically produced to be used in ethanol production. But, the other group, energy crops, are grown mostly for biofuel production. This group of crops has higher yield, they need less agrochemical inputs, less water and have low moisture content as well as high intensity of cultivation [15]. Moreover, they can be planted and grown in different types of lands and there are still many opportunities for potential improvement including expanding wildlife habitat, increasing land use diversity as well as reduced purchase cost of feedstocks [6, 16]. Some LCA studies have assessed the environmental performance of ethanol production from switchgrass, miscanthus, willow, poplar, triticale grain, giant reed, cynara and many others [6, 10, 17, 18].

Most of LCAs have found a net reduction in GHG emissions and fossil energy consumption compared to gasoline [2-4]. But there are always dissimilarities among the results of ethanol LCAs. These differences arise because there is not one single method for selecting methodological choices such as system boundaries, allocation procedures and environmental impact categories. This trade-offs compromise poses a challenge for LCA studies. Some LCA-based methodologies and their main results for ethanol production are summarized in

Table 1.

Table 1. The selected methodological choices and the main contribution of some ethanol LCAs

Author	LCA-based methodology			Main result
	System boundary	Environmental impact category	Allocation procedure	
Sheehan et al. [2004]	Cradle-to-grave	Energy, GHGs emissions, Pollution assessments	System expansion	The answer to the question of whether stover is a sustainable source of energy for transportation is highly dependant on the chosen methodology.
Kemppainen et al. [2005]	Cradle-to-gate	Global warning, smog formation, ozone depletion, acid rain, human inhalation and ingestion toxicity, human carcinogenic inhalation and ingestion toxicity, fish toxicity	physical allocation	The environmental impacts of ethanol are highly depends on the indicators used for the assessment.
Bernesson et al.[2006]	Cradle-to-grave	Global warming, acidification, eutrophication and photochemical ozone creation	System expansion, physical and economic allocation	The results were dependent on the allocation method used between the ethanol fuel and co-product.
Curran [2007]	Cradle-to-grave	Acidification, ecotoxicity, eutrophication, global warming, human health cancer, human health criteria, human health non-cancer, ozone depletion, and photochemical smog	Physical and economic allocation	The results of the LCA study are highly depended on the method which is based on the case study and assumptions.
Leng et al.[2008]	Cradle-to-grave	GHGs (CO2, CH4), Energy use (BTU), Air quality (CO, NOx)	System expansion and economic allocation	Use of different allocation approaches can have significant impacts on calculated biomass ethanol fuel-cycle energy use and energy efficiency.

Although most of these studies aim to assess the environmental performance of ethanol production, several differences can be found in the results based on the environmental evaluation metrics used in these LCA studies. The development of metrics that relate environmental performance to production processes is an excellent way to introduce the goal of sustainability into decision-making. This is a major challenge and there is a clear need for this area to develop a methodology for both LCA-based and other environmental metrics in order to have an appropriate comparison between different feedstocks for ethanol production.

Some available environmental indicators and metrics were reviewed by Menichetti et al. [19]. Because of impeded data around methodological choices and background assumptions, the grouping of evaluation metrics was not done clearly in this study. Besides, no base case for ethanol production was assessed in the LCA study done by Menichetti et al. in order to find the most suitable environmental evaluation metrics.

Another source of uncertainty for decision-makers is the source of data used in the study. The uncertainties of collected data should be assessed in an LCA study because they are important aspects for decision-makers to judge the significant of differences in ethanol production. Since determining the statistical function of data is time consuming, it is necessary to handle it in a more efficient way.

USEPA (U.S. Environmental Protection Agency) recently releases a report mentioning about some important uncertainties for clean energy. It is concluded that the assumptions about availability of technology, institutional design issues such as measurement; monitoring and verification requirements influence the evaluation results [28].

In this study, the methodology which is used for data classification is done by Heijungs [29]. In this methodology, it is proposed a categorisation of data and distinguishes data according to their uncertainty and their contribution to the results. This methodology is shown in Figure 1.

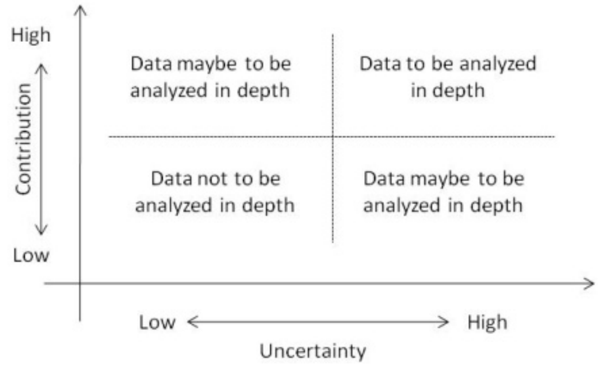

Figure 1. Data classification [Heijungs]

According to this approach illustrated in Figure 1, the limit between low and high uncertainty was defined as a data quality indicator and the one between low and high contribution was defined as 10% based on the work done by Maurice et al. [26].

Objective

The objectives of this paper are a) to apply a systematic LCA methodology to disparate biorefinery scenarios, and b) To compare the environmental impacts of ethanol production from different feedstocks including triticale and woodchips in greenfield and retrofit scenarios.

Methodology

In this study four different ethanol production scenarios were selected in order to compare their environmental performance according to the appropriate evaluation metrics developed by a base case. The base case scenario is selected in order to apply the methodology, calculate the evaluation metrics and analyse the results. The next step is expansion of the appropriate LCA-based methodology to all scenarios for ethanol production for the comparison of their environmental performance.

Biorefinery scenarios for LCA evaluation

Triticale straw, woodchips and hemicelluloses are selected for ethanol production in this assessment. Triticale which is a man made cereal crop developed by crossing wheat with rye has adapted widely in western Canada. It has a higher grain yield even in unfavourable conditions, better resistance to soil-climate conditions and tolerance to dryness, requires lower nutrient substances and fertilizer [20, 21]. Moreover, it is a local biomass in Canada; as a result it could be a reasonable source for ethanol production. Woodchips are another opportunity for ethanol production because they are currently used in pulp and paper mills in Canada. The selection of these feedstocks enables us to compare the environmental performance of ethanol production in different greenfield and retrofit scenarios.

Table 2 shows the selected pathways in this study.

Table 2. Selected ethanol pathways

Feedstock	Terms used in this study
Greenfield, Triticale straw	GF: T/S
Greenfield, Woodchips	GF: W/C
Retrofit, Woodchips	RF: W/C
Retrofit, Hemicellulose (Value Prior Pulping)	RF: VPP

The process data employed in Greenfield triticale straw and woodchips pathways is based on the process simulation done by NREL (National Renewable Energy Laboratory). This process begins with a feed handling section, where the raw material is washed and reduced in size. Then hemicellulose sugars are released by using dilute acid hydrolysis in the pre-treatment area and the hydrolyzate stream is split to be used in the fermentation step. The cellulase enzymes are produced in the cellulase enzyme production area and sent to fermentation reactors. The produced ethanol is purified by distillation and stored in the storage area. There is also the waste water section which treats the bottom streams of distillation. The solids from the process and biogas generated in the waste water treatment are burned in a combustor to provide the steam and electricity needed for the plant through a multistage turbine and generator. The remaining steam is condensed with cooling water and returned to the boiler feed water system along with the condensate from the various heat exchangers in the process. This process is energy self-sufficient and the excess electricity is sent to the grid to sale [22].

Two other processes include two different concepts of ethanol production integrated into an existing pulp mill. The retrofit woodchips process is a novel use of two processes, the first of which provides ethanol (main product) and energy (co-product) in the form of steam. This steam is then sent to the pulp mill in order to provide the additional energy required for the pulping. The pulp process is a chemical pulping process including receiving, debarking and chipping the logs followed by standard kraft pulping. It is assumed that the steam needed for the mill is produced at-site but the energy used in lime kiln comes from natural gas. The careful management of energy used in a pulp mill may actually reduce the amount of purchased fossil fuels. This could be possible by changing the type of turbine/generator in the ethanol plant in order to use the extra steam in pulp milling. More information concerning the pulping process can be found elsewhere[23].

The second concept of retrofit ethanol production is where a portion of hemicelluloses is extracted from wood chips prior to pulping and converted into ethanol while using the extracted wood chips to produce Kraft pulp for paper production. Value Prior Pulping (VPP) starts with wood extraction for hemicellulose removal, flashing of the extract to recover heat used in extraction, recycling a portion of the extract back to the extraction vessel in order to raise the solids content of the extract, sulphuric acid hydrolysis for conversion of carbohydrates into mono sugars, filtration to remove lignin, liquid-liquid extraction to remove acetic acid and furfural followed by a liming step, fermentation of sugars for ethanol production and finally distillation of product[23]. It is assumed that the existing Kraft pulp mill produces market pulp as well as ethanol and acetic acid using the hemicellulose extraction process. By integration of the VPP process into this existing pulp mill, less white liquor is required in the cooking step. This reduction has a significant effect on the amount of energy required to operate the lime kiln because the hemicellulose extraction process uses green liquor as the solvent and the green liquor does not go to the causticization and lime cycles. Since in the near neutral hemicellulose extraction process less lime mud goes to the kiln, there will be a savings of fossil fuel consumption [23, 24].

In this study, VPP is selected as the base case scenario because there are more co-products produced in this process than in other scenarios. The co-products in this process include pulp, electricity and acetic acid. This selection gives the opportunity to expand the system boundary for all other scenarios in order to have the same baseline comparison. Other scenarios including triticale straw and woodchips through greenfield and retrofit pathways are selected as the variants in this study.

Application of LCA for base case scenario

In order to quantify and classify the environmental impacts of bioethanol production from different feedstocks, LCA was used in this study following the ISO guidelines[1]. The software used in this study is SimaPro 7.1.

The goal of this study is to evaluate the environmental performance of disparate ethanol production scenarios. The scope of this study is cradle-to-gate. The end-use of ethanol can be excluded from the study as it is always the same regardless of the ethanol fuel production pathway [25]. The functional unit of this LCA study is a combined functional unit and defined based on VPP model and consequential approach is selected by using system expansion procedre in order to avoid allocation. This approach consists of expanding the boundary to include the production of all co-products in the comparison. Using this approach, the functional unit is defined based on the amount of co-products produced for 1 MJ of ethanol. These co-products include pulp, acetic acid and electricity. The system expansion approach gives the opportunity that no allocation procedure is required to split the environmental impacts between ethanol and co-products. This approach also includes other systems which would be affected by integration of ethanol production into pulp mill [30]. As an example, the difference between produced electricity is modeled by using system expansion in consequential approach while attributional approach include only the specific amount of produced electricity within the boundary. The methodological choices used in this study for comparison of different ethanol pathways are assessed elsewhere[25].

Data in this study were collected from a variety of sources including literature, reports and some directly from the used tool SimaPro 7.1, Ecoinvent inventory database. The LCIA method used in this study is Impact 2002+ with the midpoint approach.

a. Selection of environmental evaluation metrics

As mentioned before, there are several differences in the LCA results for ethanol production. These dissimilarities arise because of different indicators used in different LCAs. As a result, selection of evaluation metrics according to the specific design conditions is essential to be able to compare the environmental performance of different ethanol production scenarios. In this study the methodology for selection of metrics is designed to be target-oriented. According to the baseline model, VPP, literature review, assumptions and data design for this process, different indicators are chosen including LCA-based metrics and other environmental metrics.

For the identification of LCA-based metrics, two methods including different impact categories (midpoint vs. endpoint) are applied to VPP baseline model. The LCA results for these two methods illustrate the midpoint indicators which have the most significant contribution in endpoint categories. The selected midpoint categories are summarized in Table 3.

Table 3 . LCA-based metrics for VPP baseline model

Midpoint category	Damage category
Respiratory inorganics	Human health
Terrestrial ecotoxicity	Ecosystem quality
Land occupation	Ecosystem quality
Global warming	Climate change
Non-renewable energy	Resources

Using energy and CO2 equivalent emission indicators enables the assessment of the reduction of GHG emission and energy consumption in different ethanol production scenarios. This is required because the pre-manufacturing of the various biomass feedstocks is different. Besides GHG emissions and energy, other environmental impacts which can arise from the production of feedstocks, production and processing of ethanol, the corresponding effects on water and soil quality, should be considered. These metrics depend on various factors including feedstock, cultivation practice, land management and downstream processing route. In all scenarios used in this study, pre-manufacturing is important for the environmental loads of toxic compounds for human health. Felling, skidding, transportation and chipping of trees and cultivation, collection, baling and loading of triticale straw result in PM2.5 formation (Particle matter which is a mixture of solid particles and liquid droplets in the air) because of fuel combustion in vehicles and in industrial facilities. These activities also release toxic compounds into the ecosystem. As a result, respiratory inorganics (Human health) and terrestrial ecotoxicity (ecosystem quality) are selected as other potential metrics for the environmental evaluation in this study. Land occupation is also important because growing different feedstocks for ethanol production requires different quantity of arable lands.

Other environmental metrics are also possible depending on the goal and scope of the study and the availability of appropriate data. They are also justified because they are defined globally and accepted internationally. The selected metrics include mass intensity, energy efficiency and energy allocated for ethanol. All environmental evaluation metrics include cradle-to-gate life-cycle inventories. The fossil fuels include natural gas, gasoline and diesel used in cultivation of raw material to the end of the ethanol production stage. The products include ethanol, electricity, pulp and acetic acid. The amount of energy input and output and mass input and output for VPP process is summarized in Table 4 and Table 5.

Table 4. Energy flow for VPP baseline model

Energy input	MJ/hr
Biomass	1695835
Premanufacturing	13130
Manufacturing	74250
Energy output	MJ/hr
Ethanol	48886
Electricity	65880
Pulp	802506
Acetic acid	27246

Table 5. Mass flow for VPP baseline model

Raw material (Kg/hr)	Output (Kg/hr)		
	Ethanol	Pulp	Acetic acid
99755	1646	41667	1879

According to the Table 4 and Table 5, the results of three metrics for VPP process are shown in Table 6.

Table 6. Other environmental metrics for VPP baseline model

Metrics	VPP baseline model
Mass intensity %	45
Energy Efficiency %	53
MJ of fossil fuels/MJ of ETOH	1.82

According to the results VPP baseline model, 45 percent of the mass of raw material is converted into the products including ethanol, pulp and acetic acid. Electricity is not assumed in this metric. With respect to energy efficiency, it is concluded that 53 percent of energy content of biomass and fossil fuels used in the VPP process is converted into the ethanol and electricity. However this process consumes the highest MJ of fossil fuels for production of 1 MJ of ethanol by allocating based on mass balances.

b. Identification of key parameters

In order to draw conclusions, explain limitations and give recommendations based on the inventory results, key parameters should be defined for sensitivity and scenario analyses. It is important to systematically select key parameters. As explained before, for the selection of key parameters, the approach proposed by Maurice et al. is used in this study [26]. This methodology was described earlier. The methodology for selection of key parameters is applied to VPP model and the steps are defined in the following:

- Calculation of the contribution of total indicator results which is added per substances in VPP process
- Calculation of the contribution of unit processes on the total emission of each substance selected in the first step
- Calculation of the contribution of each unit process/emission pair to the category results by multiplying the contribution calculated in steps 1 and 2
- Selection of the key parameters with the contribution of more than10%

With this methodology, the selected key parameters are illustrated in the following table.

Table 7. Selected key parameters for sensitivity and scenario analyses

Unit process	Unit
Electricity production	KWh/MJ EToH
Transportation	tkm/ MJ EToH
Fossil fuel	MJ/MJ EToH

Transportation (distance of biomass collection) is selected for sensitivity analysis and two other parameters including electricity production and fossil fuel are chosen for the scenario analysis. Besides, according to ISO guidelines [27], another sensitivity analysis for multi-output processes is the assessment of uncertainties due to allocation rules. The mentioned sensitivity analysis is also applied in this study.

For sensitivity analysis the distance of biomass collection (transportation of biomass) is assumed to be 200 km. Other variants include 150, 300 and 500 Km for the analysis.

For the assessment of the uncertainties due to allocation rules, two allocation approaches including physical (energy content of products) and economic (market price of products) allocation are applied to the VPP process scenario. Selection of environmental contribution between ethanol and co-products based on different allocation approaches in the VPP scenario are shown in Table 8.

Table 8. Contribution of environmental burdens for VPP

Products	Contribution of environmental burdens for VPP	
	Physical allocation	Economic alocation
Ethanol	5%	2%
Electricity	7%	14%
Pulp	85%	75%
Acetic acid	3%	9%

Two key parameters for scenario analysis include the electricity production (using average Canadian grid mix) and fossil fuels (using natural gas) used in the process. The different alternatives of electricity-oriented scenario include using North American and Quebec`s electricity grid mix. Energy-oriented scenarios include using oil, coal and pellet.

Results and discussion

The methodology explained in the previous section, is applied to all ethanol scenarios in order to select the most environmental friendly ethanol production pathways.

LCA-based evaluation metrics

The characterization results for different scenarios are normalized based on VPP process as the baseline model. As a result, values less than 1 present a more environmentally friendly ethanol production scenario compared to VPP scenario. These results are presented in Figure 2.

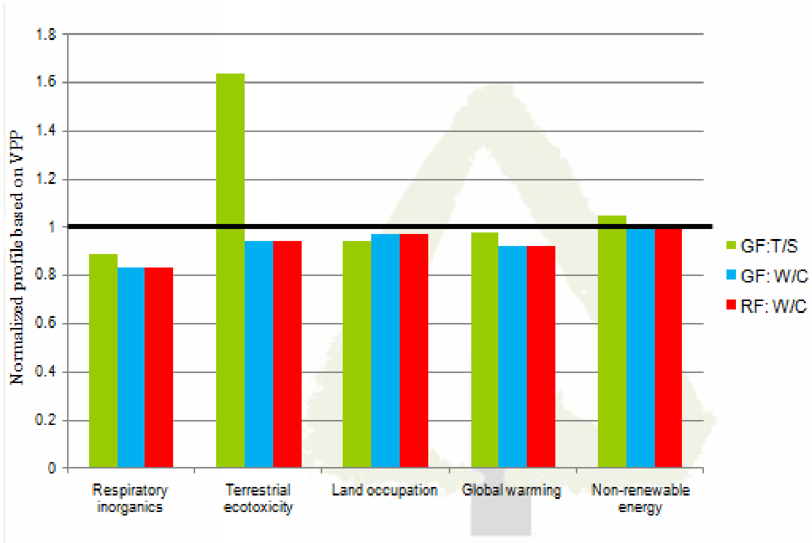

Figure 2. Normalized profile of ethanol scenarios based on VPP scenario

According to the figure, all of the ethanol pathways have a better environmental performance compared to the VPP process. Regarding the terrestrial ecotoxicity impact category, ethanol production from triticale straw is less environmentally friendly than the VPP process. This is due to heavy metals like Zinc, Chromium and Aluminum being emitted into the soil from activities during pre-manufacturing such as the baling of triticale straw. To have a better understanding of the results, interpretation is done by using sensitivity and scenario analyses. The results of these assessments are explained in the following:

a. Sensitivity analysis

Two sensitivity analyses including the selection of allocation parameters and the radius of biomass collection were applied to all ethanol scenarios. Table 9 presents the percentages of normalized results of allocation alternatives based on the selected LCA-based metrics for the production of 1 MJ ethanol through different pathways. According to the obtained results, when environmental burdens are allocated to ethanol and by-products based on the physical and economic relationship; a significant change does not occur between these two alternatives. On the other hand, by comparing the results when using allocation procedures and avoiding allocation, it is obvious that the environmental impacts associated with ethanol production done by the system expansion are the highest. Sensitivity analyses show that the allocation approach chosen influences the results more than any other parameter investigated. The difference in the environmental impact results varies up to 40% between the various allocation approaches. This occurs because of the net energy of the different ethanol scenarios and the yield of ethanol produced. However, the same trend occurs when using all of the allocation procedures for the various ethanol scenarios which can be used to select the preferred environmental scenarios.

Table 9. % Normalized results of allocation alternatives

Impact category	Physical allocation				Economic allocation			
	GF:T/S	GF: W/C	RF: W/C	RF: VPP	GF:T/S	GF: W/C	RF: W/C	RF: VPP
Respiratory inorganics	10.56	3.68	1.90	5.00	9.13	3.18	1.32	2.33
Terrestrial ecotoxicity	43.23	3.47	1.79	5.00	37.37	3.00	1.24	2.33
Land occupation	2.57	5.29	2.73	5.00	2.22	4.56	1.89	2.33
Global warming	8.71	2.66	1.37	5.00	7.53	2.30	0.95	2.33
Non-renewable energy	7.20	2.36	1.22	5.00	6.23	2.04	0.84	2.33

With respect to the radius of biomass collection, the results are illustrated in Figure 3.

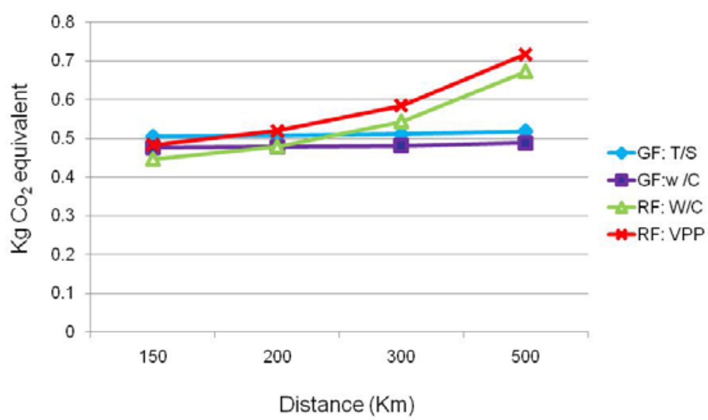

Figure 3. Sensitivity analysis of the results regarding to the distance of biomass collection

The results show that retrofit pathways are more sensitive to the radius of biomass collection compared to the greenfield pathways. It is resulted because of direct airbone emissions of gashouse substances, particulate matters and heavy metals. But in general, it is obvious that LCA results are not highly sensitive to the distance of biomass collection.

Electricity- and energy-oriented scenarios are also applied to all ethanol scenarios and the normalized profiles for global warming indicator are presented in Figure 4 and Figure 5. The normalization reference model is VPP.

Figure 4 presents the normalized profile for alternative electricity-oriented scenarios for all ethanol pathways. With respect to global warming, it is resulted that Kg CO2 equivalent emissions for triticale straw are more than 1 when using the North American electricity grid mix. This result shows that locating triticale-to-ethanol plant in North America is less environmentally friendly when compared to VPP in all electricity scenarios.

According to the type of LCA used in this study, this scenario analysis can help improve the site-selection of the ethanol plant. This could be defined based on the electricity grid mix which is used in the production of ethanol.

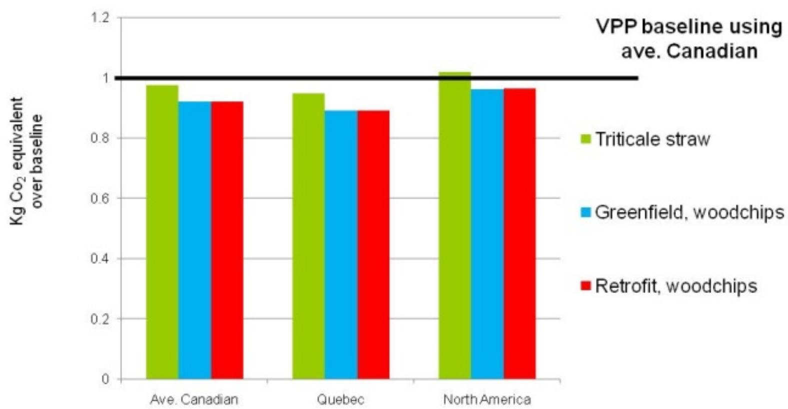

Figure 4. Normalized profile for alternative electricity-oriented scenario

According to the normalized results for the energy-oriented scenarios for global warming indicator showed in Figure 5, it is observed that in the case of retrofit ethanol production from woodchips (RF:W/C), changing the source of steam generation does not affect the results unless pellet is used as fuel. In this case, the amount of Kg CO2 equivalent emissions will change up to 30% when using pellet as the source of steam production in both ethanol production pathways. It should be noted that using pellet has a reduction of CO2 emissions but on the other hand it increases the terrestrial ecotoxicity impact category results.

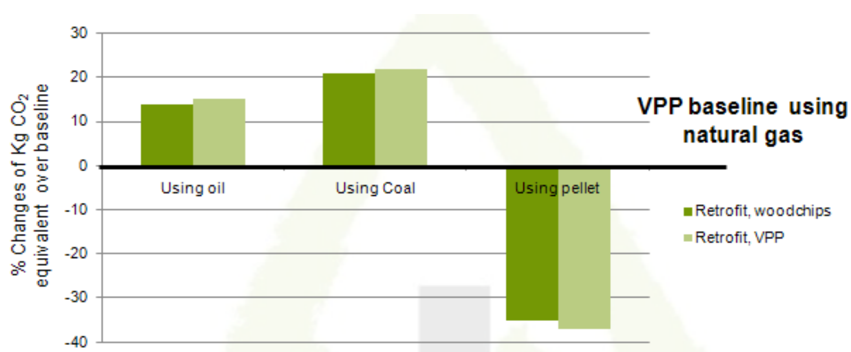

Figure 5. Normalized profile for alternative energy-oriented scenario

b. Other evaluation metrics

As explained before, mass intensity, energy efficiency and MJ of fossil fuel allocated for production of 1 MJ of ethanol are three metrics which are selected based on the goal and scope of this study.

Table **10** shows the results of these metrics for all scenarios.

Table 10. Other environmental metrics for all ethanol scenarios

Metrics	GF: T/S	GF: W/C	RF: W/C	RF: VPP
Mass intensity (%)	23	32	39	45
Energy Efficiency (%)	41	58	53	53
MJ of fossil fuels/MJ of ETOH	7.0E-04	4.8E-04	1.5E-02	1.8E+00

According to the table, VPP is the best alternative based on the mass intensity metric because it has the most products including ethanol, pulp, acetic acid and electricity among all of the ethanol scenarios. With respect to energy efficiency, greenfield and retrofit woodchips-to-ethanol and VPP pathways have the most environmentally friendly performances respectively. These two metrics make VPP an interesting choice for ethanol production; however it consumes the highest MJ of fossil fuels for production of 1 MJ of ethanol which changes the results for selection of VPP as the most environmental preferable scenario.

Greenfield pathways including triticale straw and woodchips are the best options based on the MJ of fossil fuels/MJ of ethanol metric. Due to the very small amount of fossil fuel used in the pre-manufacturing step of the mentioned models. In retrofit ethanol scenario (RF: W/C) and VPP scenario (RF:VPP), fossil fuels are used in the pre-manufacturing and the process lines. This makes them less of an environmental preferable scenario as compared to the greenfield scenarios.

Conclusion

In the application of the LCA-based methodology for all ethanol pathways, sensitivity analysis shows that the allocation approach selected influences the inventory results more than other parameters and methodological choices. The difference between results obtained by avoiding allocation (system expansion) and allocation based on physical and economic relationship indicates that environmental impacts associated with ethanol production through system expansion are highest. The final results are most sensitive to 1) the net energy of different scenarios of the ethanol production, and 2) the yield of the ethanol process.

Moreover, the additional benefit of the proposed methodology in this study is the systematical selection of LCA-based and other environmental metrics for environmental analysis of ethanol production scenarios. Indicators used for the comparison of different ethanol pathways can influence the result of the environmental evaluation strongly. Consequently, the set of metrics that can best address the environmental performance of ethanol production when comparing different pathways enhances the decision making.

Furthermore, the combination of this LCA study with other environmental tools looking at local and regional impacts improves the specific results mentioned here.

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Appendix B: Balances for different scenarios

This appendix present details about the scenarios in this study. These scenarios are illustrated through flow charts containing the main activities. At the end of the model description is presented an overall mass and energy balances.

B.1. Triticale straw-to-ethanol

B.1.1. description of the scenario

The process being analyzed here can be briefly described as using co-current dilute acid prehydrolysis of the lignocellulosic biomass with simultaneous enzymatic saccharification of the remaining cellulose and co-fermentation of the resulting glucose and xylose to ethanol. In addition to these unit operations, the process involves feedstock handling and storage, product purification, wastewater treatment, enzyme production, lignin combustion, product storage, and other utilities.

This pathway is an energy self-sufficient process. The primary feed streams including centrifuge solids, biogas and evaporator syrup are fed to a Circulating Fluidized Bed Combustor (CFBC). The small amount of waste biomass (sludge) from wastewater treatment is also sent to the burner. The solids' moisture content is reduced from 63% to 51% moisture via direct contact with flue gas exiting the burner cyclone in a drum dryer whereas the biogas and syrup enter the boiler at 4% and 60% moisture, respectively. The moisture of the combined feed to the boiler is 52%. A fan moves air into the combustion chamber. Treated water enters the heat exchanger circuit in the combustor and is evaporated and superheated to 510^{o}C (950^{o}F) and 86 atm (1265 psia) producing 235,210 kg/hr (518,550 lb/hr) of steam. Boiler efficiency, defined as the percentage of the feed heat that is converted to steam heat, is 62%. Flue gas from the dryer cyclone enters a baghouse to remove particulates, which are landfilled. The gas is exhausted through a stack. The process of producing steam needed for the ethanol production and electricity production from extra steam is illustrated in Figure B.1.

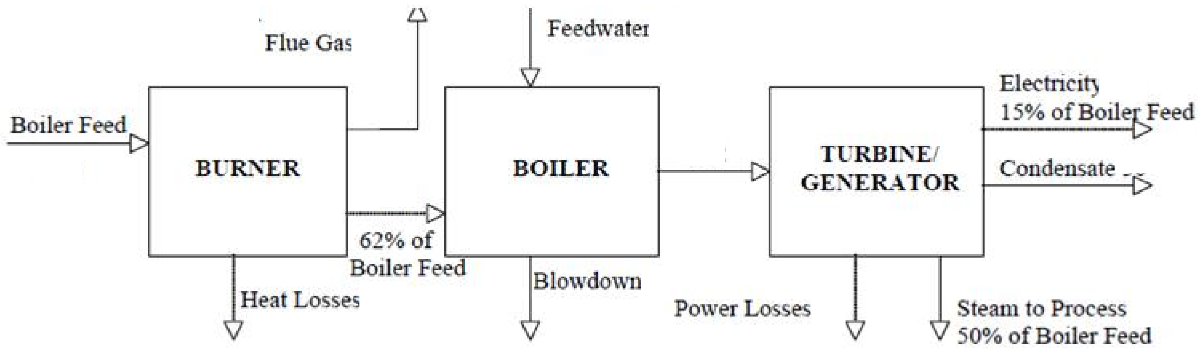

Figure B.1. CFBC/Turbogenerator for energy needed in the process

The flow chart of this process, using triticale straw for ethanol production is illustrated in Figure B.2.

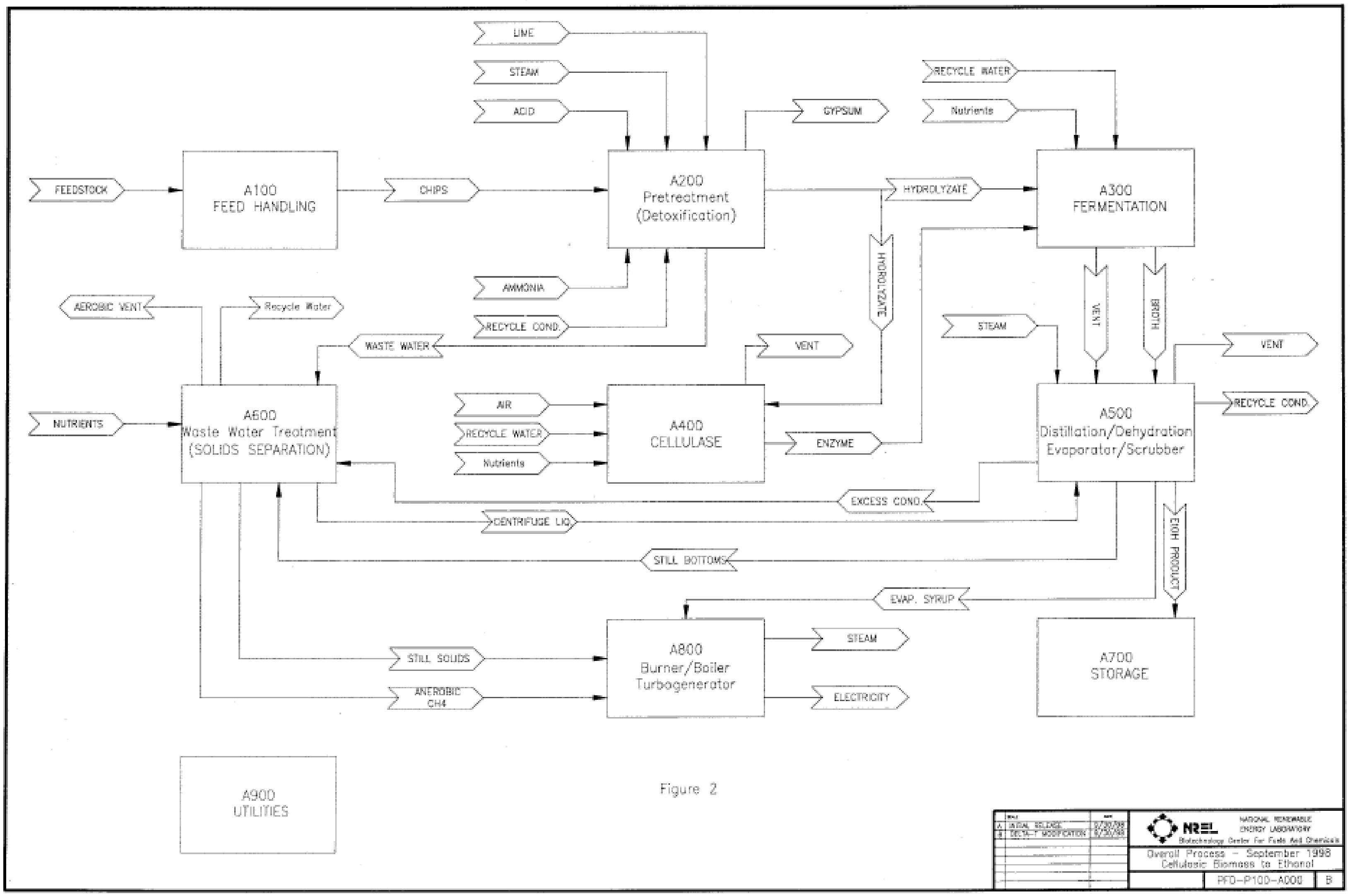

Figure B.2. Flowchart of greenfield ethanol model

B.1.2. Feedstock and its Composition

The feedstock chosen for the process design has some impact on the overall analysis. In this scenario, hardwood has been using.

Generally, the type of feedstock will have the biggest effect on the feedstock-handling portion of the process. Additionally, the feedstock composition certainly will have an impact on pre-treatment yields and on how much ethanol is produced, as well as an effect on the efficiency of the fermenting organism which depends on the presence or absence of toxic compounds.

The feedstock composition and the mass balance used for this scenario are shown in Table B.1 and Table B.2 respectively.

Table B.1. Triticale straw composition

Component	% Dry basis
cellulose	41
xylan	19
arabinan	3.5
mannan	0
galactan	2.2
acetate	3.38
lignin	18
ash	7.2
moisture	15

B.1.3. Assumptions used in this scenario

- Radius collection of triticale straw is 200 Km
- Energy required for baling and loading straw is 1.7 L/ton of straw
- Ammonia needed for the plant is transferred by rail
- Other chemical are transferred by road
- Gasoline used for product ethanol
- The efficiency for back pressure turbine is assumed 20%

Table B.2. Mass balance for triticale straw scenario (greenfield)

Scenario name: Triticale straw-to-ethanol			
Description: production of fuel grade ethanol from triticale straw			
Reference flow : 1 MJ of ethanol			
Input	**Unit/day**	**Amount**	**Note**
Materials/fuels			
Triticale straw	Ton	2400	
Hydrated lime	Ton	23.52	
Eethylenediamine tetraacetic acid(EDTA)	Ton	0.024	Used as chemical for boiler
Ammonia, liquid	Ton	35.28	
Ammonium phosphate	Ton	47.04	
Polypropylene	Ton	0.696	Used as clarifier polymer in the process
Calcium phosphate	Ton	47.04	
Diesel, burned in building machine	Ton	13.53	
Output	**Unit/day**	**Amount**	**Note**
Ethanol	Ton	540	
Electricity	KWh	8333	Energy content of ethanol = 27 MJ/Kg
Wastes and emissions			
Gypsum	Ton	70.08	Containing 19.4% water
Ash	Ton	31.848	Wood ash mixture, pure, 0% water
Carbon dioxide	Ton	403.632	

B.2. Woodchips-to-ethanol

B.2.1. description of the scenario

The process being analyzed in this scenario is exactly the same as one used in triticale straw scenario. The flow chart of this process is presented in Figure B.2.

B.2.2. Feedstock and its Composition

Here the feedstock used for ethanol production includes woodchips, specifically yellow poplar hardwood.

The feedstock composition and mass balance for the scenario are presented in Table B.3 and Table B.4 respectively.

Table B.3. Woodchips composition in greenfield pathway

Component	% Dry basis
cellulose	42.67
xylan	19.05
arabinan	0.79
mannan	3.93
galactan	0.24
acetate	4.64
lignin	27.68
ash	1
moisture	47.90

B.2.3. Assumptions used in this scenario

- Radius collection of the feedstock is 200 Km.
- Energy required for pre-manufacturing includes energy for felling, skidding, transportation and chipping
- Ammonia needed for the plant is transferred by rail
- Other chemical are transferred by road
- Gasoline used for product ethanol

Table B.4. Mass balance for woodchips scenario (greenfield)

Scenario name: Woodchips-to-ethanol			
Description: production of fuel grade ethanol from woodchips			
Reference flow : 1 MJ of ethanol			
Input	**Unit/day**	**Amount**	**Note**
Materials/fuels			
Woodchips	Ton	2000	
Lime	Ton	16.632	
Sulphuric acid	Ton	44.136	
Ammonia, liquid	Ton	28.656	
Ammonium phosphate	Ton	2.592	
Corn oil	Ton	6.432	Used as antifoam in the process
Calcium chloride	Ton	2.592	
Diesel, burned in building machine	Ton	11.28	
Output	**Unit/day**	**Amount**	**Note**
Ethanol	Ton	635	
Electricity	KWh	10942	Energy content of ethanol = 27 MJ/Kg
Wastes and emissions			
Gypsum	Ton	58.392	Containing 19.4% water
Ash	Ton	26.544	Wood ash mixture, pure, 0% water
Carbon dioxide	Ton	2829.24	

B.3. Woodchips-to-ethanol, retrofit pathway

B.3.1. description of the scenario

This process is a novel use of two processes, the first of which provides ethanol (main product) and energy (co-product) in the form of steam. This steam is then sent to the pulp mill in order to provide the additional energy required for the pulping by changing the type of generator used in the ethanol mill.

As explained in section B.1., the ethanol process is energy self-sufficient. In order to use the extra produced steam in pulp mill, a multistage turbine and generator are used. Steam is extracted from the turbine at 3 different conditions for injection into the pre-treatment reactor and heat exchange in distillation and evaporation. The careful management of the extent to which the fuel resource is used in a pulp mill may actually reduce the purchased energy provided by fossil fuels.

The flow diagram of this energy integration is illustrated in Figure B. 3.

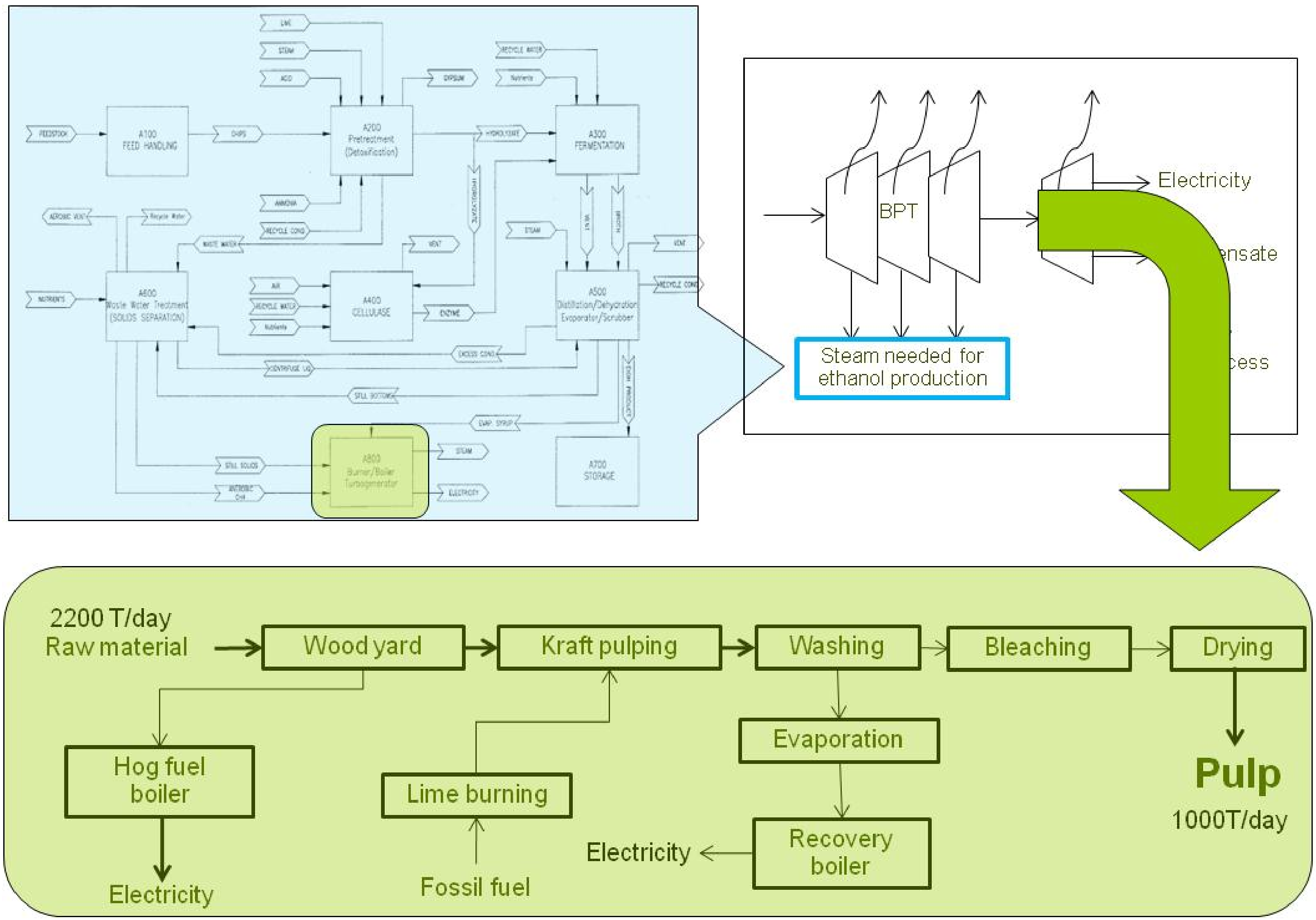

Figure B. 3. Flowchart of retrofit ethanol model (Woodchips-to-ethanol)

B.3.2. Feedstock and its Composition

The feedstock chosen for this scenario is assumed the same as the one in grreenfiled woodchips-to-ethanol production. Table B.5 shows the characterisation of different components of woodchips. The mass balance of this process is presented in Table B. 6.

Table B.5. Woodchips composition in retrofit pathway

Component	% Dry basis
cellulose	42.67
xylan	19.05
arabinan	0.79
mannan	3.93
galactan	0.24
acetate	4.64
lignin	27.68
ash	1
moisture	47.90

B.3.3. Assumptions used in this scenario

- Radius collection of the feedstock is 200 Km
- Energy required for pre-manufacturing includes energy for felling, skidding, transportation and chipping
- Ammonia needed for the plant is transferred by rail
- Other chemical are transferred by road
- Gasoline used for product ethanol
- Kraft pulp mill includes the 4 steps bleaching (DEDD)
- Natural gas is assumed as the fossil fuel for lime burning

Table B. 6. Mass balance for woodchips scenario (retrofit)

Scenario name: Woodchips-to-ethanol, retrofit			
Description: production of fuel grade ethanol from woodchips through a retrofit process			
Reference flow : 1 MJ of ethanol			
Input	**Unit/day**	**Amount**	**Note**
Resources			
Water	M^3	64000	From river
Materials/fuels			
Woodchips	Ton	4200	2200 Ton/day for ethanol plant + 2000 Ton/day for pulp mill
Lime	Ton	36.632	16.632 Ton/day for ethanol plant + 20 Ton/day for pulp mill
Sulphuric acid	Ton	44.136	For ethanol plant
Ammonia, liquid	Ton	28.656	For ethanol plant
Ammonium phosphate	Ton	2.592	For ethanol plant
Corn oil	Ton	6.432	Used as antifoam in the process of ethanol production
Calcium chloride	Ton	2.592	For ethanol plant
Diesel, burned in building machine	Ton	11.28	For ethanol plant
Sodium hydroxide	Ton	30	For pulp mill
Chlorine dioxide	Ton	25	For bleaching in pulp mill
Sodium sulphate	Ton	5	For pulp mill
Deionised water	Ton	1000	For pulp mill
Oxygen, liquid	Ton	20	For pre-lignifications in pulp mill
Magnesium sulphate	Ton	1.5	For pulp mill
Output	**Unit/day**	**Amount**	**Note**
Ethanol	Ton	635	
Pulp	Ton	1000	
Wastes and emissions			
Gypsum	Ton	58.392	Containing 19.4% water
Ash	Ton	35.544	Wood ash mixture, pure, 0% water- 26.544 Ton/day from ethanol production + 9 Ton/day from pulp mill
Carbon dioxide	Ton	5329.24	2829.24 Ton/day from ethanol production + 2500 Ton/day from pulp mill

B.4. VPP, retrofit pathway

B.4.1. Description of the scenario

Value Prior Pulping (VPP) includes the “near-neutral” hemicellulose pre-extraction integrated into an existing hardwood Kraft mill. This process starts with wood extraction for hemicellulose removal, flashing of the extract to produce steam, recycling a portion of extract back to the extraction vessel in order to raise the solids content of the extract, sulphuric acid hydrolysis for conversion of carbohydrates into mono sugars, filtration to remove lignin, liquid-liquid extraction, distillation to remove acetic acid and furfural followed by liming step, fermentation of sugars for ethanol production and finally distillation of product. It is assumed that the existing Kraft pulp mill is facilitated to produce the market pulp as well as ethanol and acetic acid using the hemicellulose extraction process. In this extraction process less white liquor is required in the cooking step. This will result in a corresponding decrease in the amount of calcium carbonate (CaCCh) that needs to be removed in the white liquor clarifier and decomposed to lime in the kiln. This reduction in flow of CaCCh has a significant effect on the amount of energy required to operate the lime kiln. This is because the hemicellulose extraction process uses green liquor (Na2C03 and Na2S) as the solvent and the green liquor does not go to the causticization and lime cycles. Since in the near neutral hemicellulose extraction process less lime mud goes to the kiln, there will be a savings of fossil fuel per day for pulp mill.

The flow chart of this process is illustrated in Figure B. 4.

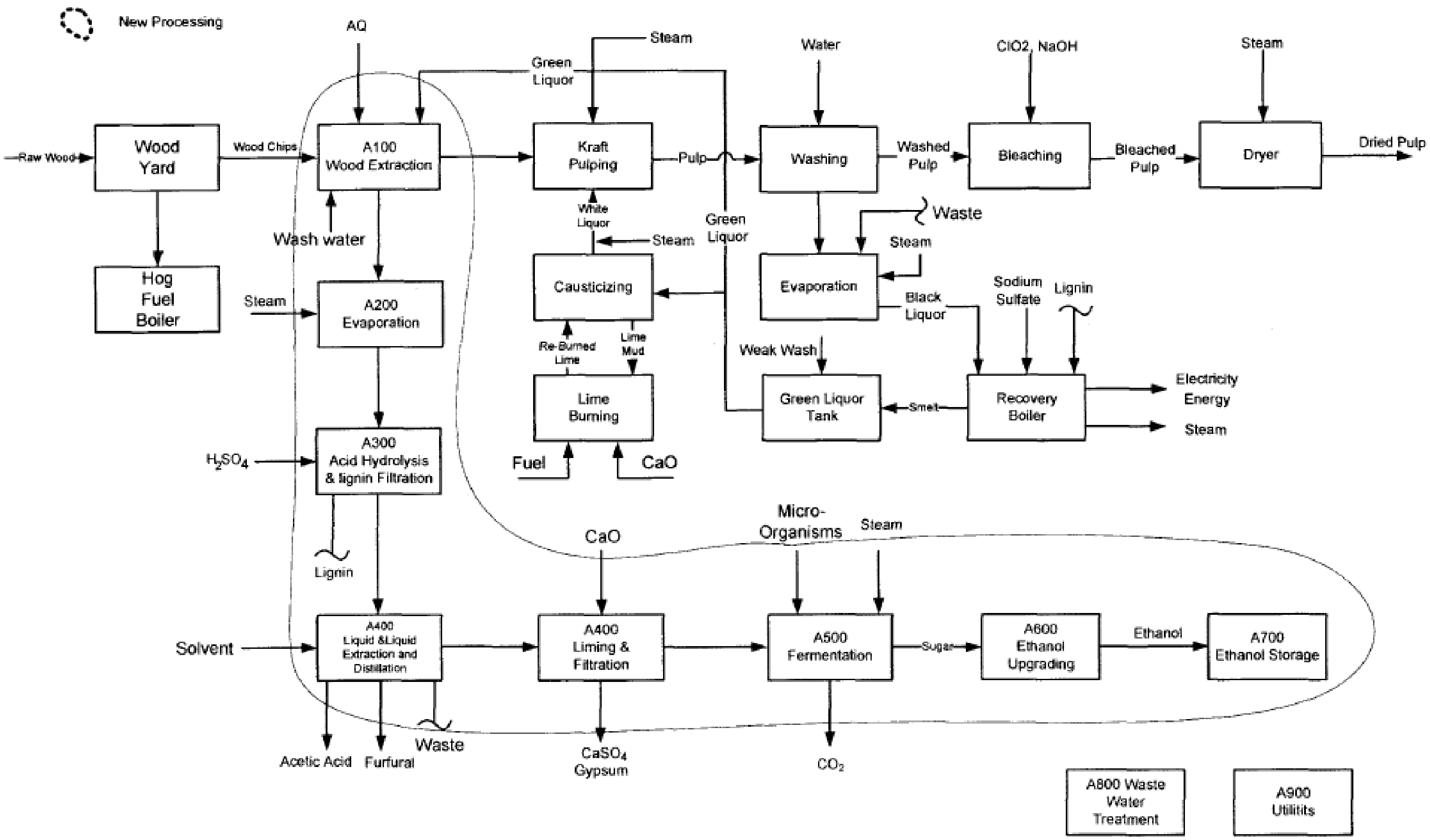

Figure B. 4. Flowchart of retrofit ethanol model (VPP)

B.4.2. Feedstock and its Composition

In this research, the feedstocks using for the VPP process is a mixed hardwood chips including birch, beech and maple.

A summative analysis on the feedstock and mass balance of the process are summarized in Table B.7 and Table B.8 respectively.

Table B.7. Woodchips composition in VPP retrofit pathway

Component		Mixed hardwood (% Weight of dry basis)
Cellulose		42.6
Hemicellulose	Arabinan	0.5
	Galactan	0.9
	Glucan	1.3
	Xylan	16.7
	Mannan	2.1
	Acetyl group	3.5
	4-O-MGA	4.6
Lignin		27.5
Ash		0.2
Moisture		50

B.4.3. Assumptions used in this scenario

- Radius collection of the feedstock is 200 Km
- Energy required for pre-manufacturing includes energy for felling, skidding, transportation and chipping
- Ammonia needed for the plant is transferred by rail
- Other chemical are transferred by road
- Gasoline used for product ethanol
- Kraft pulp mill includes the 4 steps bleaching (DEDD)
- Natural gas is assumed as the fossil fuel for lime burning
- The quantity of green liquor used after the integration of the VPP process is the same as in the base case mill

Table B.8. Mass balance for woodchips VPP scenario (retrofit)

Scenario name: Value Prior Pulping, retrofit			
Description: production of fuel grade ethanol from woodchips in through a retrofit process			
Reference flow : 1 MJ of ethanol			
Input	**Unit/day**	**Amount**	**Note**
Resources			
Water	M^3	16630	From river
Materials/fuels			
Woodchips	Ton	2400	
Lime	Ton	53.21	
Sulphuric acid	Ton	74.8	For ethanol plant
Anthraquinone	Ton	1.09	For ethanol plant
Ethyl acetate	Ton	21.14	For ethanol plant
Diesel, burned in building machine	Ton	12.41	For ethanol plant
Sodium hydroxide	Ton	30	For pulp mill
Chlorine dioxide	Ton	25	For bleaching in pulp mill
Sodium sulphate	Ton	5	For pulp mill
Deionised water	Ton	1000	For pulp mill
Oxygen, liquid	Ton	20	For pre-lignifications in pulp mill
Magnesium sulphate	Ton	1.5	For pulp mill
Output	**Unit/day**	**Amount**	**Note**
Ethanol	Ton	39.5	
Acetic acid	Ton	45.1	
Pulp	Ton	1000	
Electricity	MW	18.3	
Wastes and emissions			
Gypsum	Ton	161.8	Containing 19.4% water
Ash	Ton	0.12	Wood ash mixture, pure, 0% water
Carbon dioxide	Ton	2823.24	

B5. Energy balances for different scenarios

As mentioned before, the greenfield scenarios including triticale straw and woodchips are energy self-sufficient. The needed heat process is provided in site and the extra steam is used in a generator in order to produce electricity sent to grid mix. For this reason, using the concept of integration of an ethanol plant with an existing pulp mill reduce the amount of fossil fuels used in the pulping process. A comparison is made to the base Kraft mill case where no energy integration is in the pulping line. The comparison of energy requirement and production between existing and integrated Kraft pulp mill for a 1000 tonne per day pulp production rate is illustrate in Table B.9.

Table B.9. Energy balances for different scenarios

Different cases	Total energy needed (GJ/day)	Energy provided (GJ/day)		
		Recovery boiler	Hog fuel boiler	Fossil fuel source
Kraft mill	18	15	3	2
Woodchips-based ethanol mill integrated into a pulp mill	18	15	3	0.21
VPP	19.95	12.09	7.04	1.63

In the case of VPP, the integrated Kraft mill would produce approximately 35% less steam than the conventional Kraft mill because 10% of the wood mass is extracted and additional energy is required for the pre-evaporation and distillation operations.

Appendix C: LCA results for different scenarios

This appendix presents the LCA results for all scenarios in this study.

C.1. LCA-based metrics

Table C. 1 shows the characterised LCA results for all scenarios.

Table C. 1. Characterized LCA results for all scenarios

Impact category	Unit	GF:T/S	GF: W/C	RF: W/C	RF: VPP
Carcinogens	kg $C_2H_3Cl_{eq}$	3.70E-03	3.33E-03	3.33E-03	4.67E-03
Non-carcinogens	kg $C_2H_3Cl_{eq}$	1.16E-02	8.71E-03	8.73E-03	9.02E-03
Respiratory inorganics	kg $PM2.5_{eq}$	5.18E-04	4.82E-04	4.83E-04	5.81E-04
Ionizing radiation	Bq C-14 $_{eq}$	1.10E+01	1.09E+01	1.09E+01	1.03E+01
Ozone layer depletion	kg CFC-11 $_{eq}$	5.22E-08	4.96E-08	4.96E-08	4.81E-08
Respiratory organics	kg $C_2H_{4\ eq}$	2.53E-04	2.48E-04	2.48E-04	2.70E-04
Aquatic ecotoxicity	kg TEG water	3.42E+01	3.05E+01	3.06E+01	4.31E+01
Terrestrial ecotoxicity	kg TEG soil	1.56E+01	8.94E+00	8.95E+00	9.49E+00
Terrestrial acid/nutri	kg $SO_{2\ eq}$	1.44E-02	1.29E-02	1.29E-02	1.47E-02
Land occupation	m^2org.arable	8.95E-02	9.22E-02	9.22E-02	9.47E-02
Aquatic acidification	kg $SO_{2\ eq}$	3.10E-03	2.91E-03	2.92E-03	3.97E-03
Aquatic eutrophication	kg PO_4 P-lim	3.47E-05	2.00E-05	2.00E-05	3.83E-05
Global warming	kg $CO_{2\ eq}$	5.07E-01	4.78E-01	4.79E-01	5.19E-01
Non-renewable energy	MJ primary	9.45E+00	9.09E+00	9.10E+00	9.02E+00
Mineral extraction	MJ surplus	8.47E-03	7.75E-03	7.75E-03	9.53E-03

C.2. Sensitivity analysis

Table C.2 shows the characterization results of allocation alternatives and Table C.3 shows the characterization results of radius of biomass collection alternatives for different pathways.

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Table C.2. Characterization results of allocation alternatives for different pathways

Impact category	Unit	Physical allocation				Economic allocation			
		GF:T/S	GF: W/C	RF: W/C	RF: VPP	GF:T/S	GF: W/C	RF: W/C	RF: VPP
Carcinogens	kg C2H3Cl eq	4.99E-04	1.11E-04	5.74E-05	2.33E-04	4.32E-04	9.61E-05	3.99E-05	1.09E-04
Non-carcinogens	kg C2H3Cl eq	2.93E-03	1.32E-04	6.83E-05	4.51E-04	2.53E-03	1.14E-04	4.74E-05	2.10E-04
Respiratory inorganics	kg PM2.5 eq	5.47E-05	1.77E-05	9.15E-06	2.90E-05	4.73E-05	1.53E-05	6.35E-06	1.35E-05
Ionizing radiation	Bq C-14 eq	2.06E-01	5.68E-02	2.93E-02	5.14E-01	1.78E-01	4.91E-02	2.03E-02	2.39E-01
Ozone layer depletion	kg CFC-11 eq	4.97E-09	1.83E-09	9.44E-10	2.41E-09	4.30E-09	1.58E-09	6.55E-10	1.12E-09
Respiratory organics	kg C2H4 eq	1.79E-05	9.41E-06	4.85E-06	1.35E-05	1.55E-05	8.12E-06	3.37E-06	6.28E-06
Aquatic ecotoxicity	kg TEG water	4.46E+00	6.82E-01	3.52E-01	2.16E+00	3.85E+00	5.89E-01	2.44E-01	1.00E+00
Terrestrial ecotoxicity	kg TEG soil	6.73E+00	3.11E-01	1.60E-01	4.74E-01	5.82E+00	2.68E-01	1.11E-01	2.21E-01
Terrestrial acid/nutri	kg SO2 eq	1.91E-03	4.70E-04	2.43E-04	7.34E-04	1.65E-03	4.06E-04	1.68E-04	3.42E-04
Land occupation	m2org.arable	2.30E-03	4.87E-03	2.51E-03	4.74E-03	1.99E-03	4.21E-03	1.74E-03	2.21E-03
Aquatic acidification	kg SO2 eq	3.06E-04	1.06E-04	5.46E-05	1.98E-04	2.64E-04	9.13E-05	3.79E-05	9.24E-05
Aquatic eutrophication	kg PO4 P-lim	1.55E-05	9.82E-07	5.06E-07	1.91E-06	1.34E-05	8.47E-07	3.51E-07	8.92E-07
Global warming	kg CO2 eq	4.42E-02	1.27E-02	6.57E-03	2.60E-02	3.82E-02	1.10E-02	4.56E-03	1.21E-02
Non-renewable energy	MJ primary	6.80E-01	2.15E-01	1.11E-01	4.51E-01	5.88E-01	1.85E-01	7.69E-02	2.10E-01
Mineral extraction	MJ surplus	9.58E-04	1.94E-04	9.99E-05	4.76E-04	8.28E-04	1.67E-04	6.93E-05	2.22E-04

Table C.3. Characterization results of radius of biomass collection alternatives for different pathways

Impact category	Unit	150 Km				200 Km				300 Km				500 Km			
		GF:T/S	GF: W/C	RF: W/C	RF: VPP	GF:T/S	GF: W/C	RF: W/C	RF: VPP	GF:T/S	GF: W/C	RF: W/C	RF: VPP	GF:T/S	GF: W/C	RF: W/C	RF: VPP
Carcinogens	kg C2H3Cl eq	3.69E-03	3.32E-03	3.11E-03	4.43E-03	3.70E-03	3.33E-03	3.33E-03	4.67E-03	3.73E-03	3.35E-03	3.77E-03	5.10E-03	3.78E-03	3.40E-03	4.63E-03	5.99E-03
Non-carcinogens	kg C2H3Cl eq	1.15E-02	8.69E-03	8.38E-03	8.65E-03	1.16E-02	8.71E-03	8.73E-03	9.02E-03	1.16E-02	8.75E-03	9.42E-03	9.72E-03	1.17E-02	8.82E-03	1.08E-02	1.11E-02
Respiratory inorganics	kg PM2.5 eq	5.15E-04	4.79E-04	4.34E-04	5.28E-04	5.18E-04	4.82E-04	4.83E-04	5.81E-04	5.24E-04	4.87E-04	5.79E-04	6.77E-04	5.36E-04	4.98E-04	7.73E-04	8.77E-04
Ionizing radiation	Bq C-14 eq	1.10E+01	1.09E+01	1.08E+01	1.01E+01	1.10E+01	1.09E+01	1.09E+01	1.03E+01	1.10E+01	1.09E+01	1.12E+01	1.05E+01	1.10E+01	1.09E+01	1.17E+01	1.11E+01
Ozone layer depletion	kg CFC-11 eq	5.19E-08	4.93E-08	4.45E-08	4.25E-08	5.22E-08	4.96E-08	4.96E-08	4.81E-08	5.28E-08	5.02E-08	5.99E-08	5.84E-08	5.41E-08	5.13E-08	8.05E-08	7.95E-08
Respiratory organics	kg C2H4 eq	2.52E-04	2.46E-04	2.20E-04	2.39E-04	2.53E-04	2.48E-04	2.48E-04	2.70E-04	2.57E-04	2.51E-04	3.04E-04	3.25E-04	2.64E-04	2.57E-04	4.16E-04	4.41E-04
Aquatic ecotoxicity	kg TEG water	3.41E+01	3.04E+01	2.87E+01	4.11E+01	3.42E+01	3.05E+01	3.06E+01	4.31E+01	3.44E+01	3.07E+01	3.42E+01	4.68E+01	3.49E+01	3.11E+01	4.16E+01	5.44E+01
Terrestrial ecotoxicity	kg TEG soil	1.55E+01	8.88E+00	7.75E+00	8.18E+00	1.56E+01	8.94E+00	8.95E+00	9.49E+00	1.57E+01	9.07E+00	1.13E+01	1.19E+01	1.60E+01	9.33E+00	1.61E+01	1.68E+01
Terrestrial acid/nutri	kg SO2 eq	1.43E-02	1.29E-02	1.14E-02	1.30E-02	1.44E-02	1.29E-02	1.29E-02	1.47E-02	1.46E-02	1.31E-02	1.60E-02	1.77E-02	1.49E-02	1.34E-02	2.22E-02	2.41E-02
Land occupation	m2org.arable	1.28E-01	9.22E-02	9.20E-02	9.44E-02	1.28E-01	9.22E-02	9.22E-02	9.47E-02	1.28E-01	9.22E-02	9.28E-02	9.53E-02	1.28E-01	9.23E-02	9.38E-02	9.63E-02
Aquatic acidification	kg SO2 eq	3.09E-03	2.90E-03	2.69E-03	3.72E-03	3.10E-03	2.91E-03	2.92E-03	3.97E-03	3.13E-03	2.94E-03	3.37E-03	4.42E-03	3.19E-03	2.99E-03	4.28E-03	5.35E-03
Aquatic eutrophication	kg PO4 P-lim	3.46E-05	1.99E-05	1.81E-05	3.62E-05	3.47E-05	2.00E-05	2.00E-05	3.83E-05	3.50E-05	2.02E-05	2.38E-05	4.21E-05	3.54E-05	2.06E-05	3.14E-05	4.99E-05
Global warming	kg CO2 eq	5.05E-01	4.76E-01	4.46E-01	4.84E-01	5.07E-01	4.78E-01	4.79E-01	5.19E-01	5.11E-01	4.82E-01	5.43E-01	5.84E-01	5.19E-01	4.89E-01	6.73E-01	7.18E-01
Non-renewable energy	MJ primary	9.41E+00	9.06E+00	8.56E+00	8.43E+00	9.45E+00	9.09E+00	9.10E+00	9.02E+00	9.51E+00	9.15E+00	1.02E+01	1.01E+01	9.65E+00	9.26E+00	1.23E+01	1.23E+01
Mineral extraction	MJ surplus	8.45E-03	7.74E-03	7.50E-03	9.25E-03	8.47E-03	7.75E-03	7.75E-03	9.53E-03	8.50E-03	7.78E-03	8.27E-03	1.00E-02	8.56E-03	7.83E-03	9.31E-03	1.11E-02

C.3. Scenario analysis

Table C.4 and Table C.5 how the inventory analyses for electricity- and energy-oriented scenarios for all ethanol pathways respectively.

Table C.4. Inventory results for alternative electricity-oriented scenario for all ethanol pathways

Impact category	Unit	Average Canadian				North America				Quebec			
		GF:T/S	GF: W/C	RF: W/C	RF: VPP	GF:T/S	GF: W/C	RF: W/C	RF: VPP	GF:T/S	GF: W/C	RF: W/C	RF: VPP
Carcinogens	kg C2H3Cl eq	3.70E-03	3.33E-03	3.33E-03	4.67E-03	3.77E-03	3.41E-03	3.41E-03	4.67E-03	3.66E-03	3.29E-03	3.29E-03	4.67E-03
Non-carcinogens	kg C2H3Cl eq	1.16E-02	8.71E-03	8.73E-03	9.02E-03	1.21E-02	9.21E-03	9.24E-03	9.02E-03	1.13E-02	8.42E-03	8.42E-03	9.02E-03
Respiratory inorganics	kg PM2.5 eq	5.18E-04	4.82E-04	4.83E-04	5.81E-04	5.30E-04	4.94E-04	4.95E-04	5.81E-04	5.07E-04	4.71E-04	4.71E-04	5.81E-04
Ionizing radiation	Bq C-14 eq	1.10E+01	1.09E+01	1.09E+01	1.03E+01	1.15E+01	1.14E+01	1.15E+01	1.03E+01	1.02E+01	1.01E+01	1.02E+01	1.03E+01
Ozone layer depletion	kg CFC-11 eq	5.22E-08	4.96E-08	4.96E-08	4.81E-08	5.28E-08	5.02E-08	5.03E-08	4.81E-08	5.14E-08	4.88E-08	4.87E-08	4.81E-08
Respiratory organics	kg C2H4 eq	2.53E-04	2.48E-04	2.48E-04	2.70E-04	2.55E-04	2.50E-04	2.50E-04	2.70E-04	2.52E-04	2.47E-04	2.47E-04	2.70E-04
Aquatic ecotoxicity	kg TEG water	3.42E+01	3.05E+01	3.06E+01	4.31E+01	3.48E+01	3.11E+01	3.12E+01	4.31E+01	3.37E+01	3.01E+01	3.01E+01	4.31E+01
Terrestrial ecotoxicity	kg TEG soil	1.56E+01	8.94E+00	8.95E+00	9.49E+00	1.57E+01	9.03E+00	9.04E+00	9.49E+00	1.55E+01	8.89E+00	8.89E+00	9.49E+00
Terrestrial acid/nutri	kg SO2 eq	1.44E-02	1.29E-02	1.29E-02	1.47E-02	1.47E-02	1.33E-02	1.33E-02	1.47E-02	1.41E-02	1.27E-02	1.27E-02	1.47E-02
Land occupation	m2org.arable	8.95E-02	9.22E-02	9.22E-02	9.47E-02	8.96E-02	9.23E-02	9.23E-02	9.47E-02	8.94E-02	9.22E-02	9.22E-02	9.47E-02
Aquatic acidification	kg SO2 eq	3.10E-03	2.91E-03	2.92E-03	3.97E-03	3.19E-03	3.00E-03	3.01E-03	3.97E-03	3.04E-03	2.84E-03	2.84E-03	3.97E-03
Aquatic eutrophication	kg PO4 P-lim	3.47E-05	2.00E-05	2.00E-05	3.83E-05	3.49E-05	2.01E-05	2.02E-05	3.83E-05	3.46E-05	1.98E-05	1.98E-05	3.83E-05
Global warming	kg CO2 eq	5.07E-01	4.78E-01	4.79E-01	5.19E-01	5.29E-01	5.00E-01	5.01E-01	5.19E-01	4.92E-01	4.63E-01	4.63E-01	5.19E-01
Non-renewable energy	MJ primary	9.45E+00	9.09E+00	9.10E+00	9.02E+00	9.78E+00	9.42E+00	9.45E+00	9.02E+00	9.15E+00	8.79E+00	8.79E+00	9.02E+00
Mineral extraction	MJ surplus	8.47E-03	7.75E-03	7.75E-03	9.53E-03	8.48E-03	7.77E-03	7.77E-03	9.53E-03	8.45E-03	7.74E-03	7.74E-03	9.53E-03

Table C.5. Inventory results for alternative energy-oriented scenario for all ethanol pathways

Impact category	Unit	Natural gas		Oil		Coal		Pellet	
		RF: W/C	RF: VPP	RF: W/C	RF: VPP	RF: W/C	RF: VPP	RF: W/C	RF: VPP
Carcinogens	kg C2H3Cl eq	3.33E-03	4.67E-03	3.30E-03	4.63E-03	3.30E-03	4.63E-03	3.30E-03	4.63E-03
Non-carcinogens	kg C2H3Cl eq	8.73E-03	9.02E-03	8.74E-03	9.04E-03	8.85E-03	9.15E-03	8.83E-03	9.13E-03
Respiratory inorganics	kg PM2.5 eq	4.83E-04	5.81E-04	4.84E-04	5.82E-04	4.88E-04	5.87E-04	4.85E-04	5.83E-04
Ionizing radiation	Bq C-14 eq	1.09E+01	1.03E+01	1.10E+01	1.03E+01	1.10E+01	1.03E+01	1.10E+01	1.03E+01
Ozone layer depletion	kg CFC-11 eq	4.96E-08	4.81E-08	4.97E-08	4.82E-08	4.89E-08	4.73E-08	4.89E-08	4.74E-08
Respiratory organics	kg C2H4 eq	2.48E-04	2.70E-04	2.49E-04	2.70E-04	2.47E-04	2.69E-04	2.47E-04	2.69E-04
Aquatic ecotoxicity	kg TEG water	3.06E+01	4.31E+01	3.07E+01	4.33E+01	3.11E+01	4.37E+01	3.12E+01	4.38E+01
Terrestrial ecotoxicity	kg TEG soil	8.95E+00	9.49E+00	8.98E+00	9.52E+00	9.07E+00	9.62E+00	9.19E+00	9.74E+00
Terrestrial acid/nutri	kg SO2 eq	1.29E-02	1.47E-02	1.30E-02	1.47E-02	1.31E-02	1.48E-02	1.30E-02	1.47E-02
Land occupation	m2org.arable	9.22E-02	9.47E-02	9.22E-02	9.47E-02	9.23E-02	9.47E-02	9.24E-02	9.49E-02
Aquatic acidification	kg SO2 eq	2.92E-03	3.97E-03	2.92E-03	3.98E-03	2.96E-03	4.02E-03	2.92E-03	3.97E-03
Aquatic eutrophication	kg PO4 P-lim	2.00E-05	3.83E-05	2.04E-05	3.87E-05	2.00E-05	3.83E-05	2.03E-05	3.86E-05
Global warming	kg CO2 eq	4.79E-01	5.19E-01	4.80E-01	5.21E-01	4.81E-01	5.22E-01	4.75E-01	5.16E-01
Non-renewable energy	MJ primary	9.10E+00	9.02E+00	9.10E+00	9.02E+00	9.08E+00	9.00E+00	9.03E+00	8.94E+00
Mineral extraction	MJ surplus	7.75E-03	9.53E-03	7.77E-03	9.54E-03	7.75E-03	9.52E-03	7.75E-03	9.53E-03

Appendix D: Studying the consequences of different system choices in LCA for ethanol production: An assessment

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Abstract

Ethanol derived from biomass is increasingly preferred as a fuel for environmental reasons and possible economical potential. Different kinds of feedstocks including sugar, starch and cellulose could be used for ethanol production. As the conversion of different feedstocks to ethanol is associated with various co-products and tillage activities it is not obvious which methodological framework can analyse the environmental performance of ethanol production appropriately. Life cycle assessment (LCA) is recognized as a systematic and practical approach to the implementation of the lifecycle thinking concept in sustainable design. However, different LCA methodological aspects such as system boundaries, allocation approaches for multifunctional processes and considered environmental impacts should be chosen carefully to obtain an appropriate evaluation of ethanol production. It is obvious that there is not one single way to make the methodological choices but it is important to consider the consequences which different methodological choices have on the results.

As the objective of this paper is to assess a body of knowledge related to ethanol LCA studies in order to identify some of the methodological choices and their consequences in the final result, it focuses on a survey of 26 LCA studies concerning the production of ethanol from different feedstocks. A critical review of the strengths and weaknesses of different approaches was done to determine the impact of the selection of different methodological choices on the results. We did not correct the differences but we compared the obtained results and the consequences of each of these selections including system boundaries, allocation procedures and environmental

impact categories in the respective LCA publications. To assess the performance of different methodological choices in an LCA, a base case needs to be defined. The base case was selected to be the same as the one used in the LCA study done by Kemppainen et al. [2005] based on the process simulation by National Renewable Energy Laboratory (NREL). This enables us to compare different methodologies in order to assess their consequences and propose an appropriate one for ethanol production case study assessments.

D.1. Introduction

More recently, the global warming problem has been increasingly a focus of attention and greater use of bio-fuels, which have been able to compete with petroleum-based fuels in the environmental issues [1, 2].

It is important that production of ethanol from all biomass feedstocks including sugar, starch and cellulose, have environmental advantages over fossil fuels. Sugar and starch-based feedstocks have been until now the primary raw materials for ethanol production, but competing food and feed demands and prices will eventually limit the expansion of sugar- and starch-based ethanol production. Since cellulosic biomass conversion to ethanol has the possibility of so many benefits, research should be improved the environmental efficiency of this group as well as economic and social aspects in order to have a sustainable future for ethanol production[3, 4]

LCA is a technique that allows the evaluation of environmental performance of ethanol production. But selection of the best alternative methodological choices is necessary in order to improve the environmental assessment of ethanol production from different feedstocks.

This study begins with the reviewing of twenty six LCA studies focusing on different methodological choices for ethanol production. It enables us to recognize, characterize and analyze the most important alternatives in an LCA methodology as well as to identify the strengths and weaknesses of each LCA methodological approach.

D.2. Life Cycle Assessment

Life cycle assessment (LCA) is recognized as a systematic and practical approach to the implementation of lifecycle thinking concept in sustainable design. It is defined as the "compilation and evaluation of the inputs, outputs and the potential environmental impacts of a product system throughout its life cycle" [5]. By taking into considerations of all the stages of the product lifecycle through design, LCA is intended to incorporate environmental factors into early design phases to support design option comparison and to improve identification of potential of different options, such as raw material selections, manufacturing process methods, recycling strategies, or revealing of environmental profiles [5].

ISO 14040 [5] recommends a standard LCA methodological framework including the steps for goal and scope definition, inventory analysis, impact assessment, and interpretation. In the goal and scope, the reasons why we are doing this study, the intended audience and the activities included and excluded in the study are defined. After this step, carrying out a LCA continues with collection of data and details, this is called inventory analysis. This life cycle inventory includes all resource inputs and environmental outputs for each process and technology which is modeled in assessment step. The results of this modeling vary widely according to the assumptions and methods used in the study. It is clear that there are many ways for selecting methodological choices and there is not one single method to have a general solution for that. The important consideration is to assess the consequences which different methodology has in the final results.

D.3. Literature review

This paper focuses on a survey of 26 LCA studies concerning the production of ethanol from first and second generation feedstocks. These studies, published between 2001 and 2008, were reviewed to develop an overall picture of LCA evaluation for ethanol production. One of the important criteria for the selection of these publications was that the LCA methodology used in these assessments was described and several environmental impact categories were used. They were also selected based on their allocation procedures associated with various co-products in ethanol production. A critical review of the strengths and weaknesses of different approaches was done to determine the impact of these selections on the results. These reviewed LCAs reported in this study include two kinds of feedstocks for ethanol production:

- First generation: corn grain, cassava, sugar beet, wheat grain and sugarcane
- Second generation: agricultural and forest residues, wood and municipal solid waste

Table D.1. The summary of reviewed articles

References	Country	Feedstock	Main conclusion
Panray Beeharry [2001]	Mauritius	sugarcane	Sugarcane bioenergy systems stand out as promising energy projects for environment.
Kadam [2002]	India	Bagasse	Converting of bagasse to ethanol generally has less environmental impacts in compare to burring it. [7]
Kim et al. [2002]	US	Corn	Sensitivity analyses show that the choice of allocation procedures has the greatest impact on fuel ethanol net energy. [8]
Fu et al. [2003]	Canada	Agricultural and forest wood waste	The reduction of GHGs by using biofuel is particularly sensitive to the source of energy used to produce the process steam. [9]
Durante et al.[2004]	US	Corn	Ethanol reduces greenhouse gas emissions compared to conventional gasoline.[10]
Sheehan et al. [2004]	US	Corn stover	The answer to the question of whether stover is a sustainable source of energy for transportation is highly depended on the chosen methodology. [11]
Kemppainen et al. [2005]	US	Virgin timber and recycled newsprints	The environmental impacts of ethanol are highly depends on the type of feedstocks. [3]
Kim et al. [2005]	US	Corn	The energy consumed in ethanol production is smaller than the energy content of ethanol. [12]
Hu et al.[2006]	China	Cassava	Environmental emissions of the cassava-based ethanol are changeable based on the design variables.[13]
Malca et al.[2006]	France	Sugar beet or Wheat	The optimum use of co-products in ethanol production is needed to improve the energy efficiency.[2]
Kim et al. [2006]	US	Corn	Using ethanol in the form of E_{10} and E_{85} has different performance based on the chosen environmental impacts.[14]
Bernesson et al.[2006]	Sweden	Winter wheat	The results were dependent on the allocation method used between the ethanol fuel and co-product. [15]
Botha et al. [2006]	South Africa	Bagasse	Using fuel ethanol has better results in term of environmental impacts.[16]
Baral et al.[2006]	US	corn	Ethanol has lower returns on energy investment (rE) in comparison to gasoline.[17]

Fleming et al.[2006]	US	cellulose (woody, herbaceous)	The biofuel options hold the potential for significant reductions in non-renewable energy use and GHG emissions compared to gasoline/diesel fuel.[18]
Hill et al.[2006]	US	Corn	Energy conservation of non-food biofuel has better environmental benefits over the longer term. [19]
Reijnders et al.[2007]	Europe	Sugar beet, wheat grain	Presently, there is a trades-off between lignocellulosic crops and starch or sugar derived ethanol regarding life cycle fossil fuel inputs or greenhouse gas emissions.[20]
Beer et al.[2007]	Australia	wheat starch and from C-molasses and cellulose	Using of ethanol has demonstrable greenhouse gas benefits in both light and heavy vehicles.[21]
Weiss et al.[2007]	Germany	Non-food based biomass	The results of this study demonstrate that the potential of bio-based products to reduce negative environmental impacts compared to their fossil counterparts strongly depends on the assumptions used in the methodology.[22]
Wismer et al. [2007]	Canada	wood residue, Hybrid poplar(HP)	Bio-ethanol as a gasoline/ethanol blend is an important means to reduce greenhouse gas emissions.[23]
Curran [2007]	US	corn grain	The results of the LCA study are highly depended on the allocation methodology which is based on the case study and assumptions.[24]
Kalogo et al. [2007]	US	MSW (Paper, wood, yard waste)	Producing ethanol from MSW can contribute to reducing dependence on non-renewable petroleum resources and reducing GHG emissions.[25]
Gabrielle et al. [2008]	Europe	Wheat straw	The factors of calculation the environmental impacts should be addressed based on local characteristics rather than on national or global averages.[26]
Nguyen et al. [2008]	Thailand	Cassava	Ethanol used in form of E_{10} or E_{85} helps the reduction of energy use and GHG emissions but its conversion step is the main source of energy use and most environmental impacts. [27]
Kim et al. [2008]	US	Corn	Using ethanol E_{10} derived from corn would reduce non-renewable energy and greenhouse gas emissions but would increase acidification, eutrophication and photochemical smog, compared to using gasoline as liquid fuel. [28]
Leng et al.[2008]	China	Cassava	Use of different allocation approaches can have significant impacts on calculated biomass ethanol fuel-cycle energy use and energy efficiency. [29]

As it is summarized in the table, many LCAs discuss about the different methodological choices such as system boundaries, environmental impact category and allocation procedures and their consequences on the results because of fundamental differences in modelling [6, 8, 9, 11, 13-16, 22, 24, 26-29]. Most of dissimilarities in ethanol LCAs arise because there is not one single methodology for selecting these choices. The selection of these choices is the key issue which have to be identified and adapted in ethanol LCA studies. This is the driving force of this study. In the following sections, each of these selections are described in details.

D.3.1. System boundaries

One of the methodological choices in each LCA study is selecting the system boundary under the terms of goal and scope. It consists of the activities included and/or excluded in the study. The system boundary should be set in order to include all important environmental burdens in the system such as energy production used for converting biomass to ethanol, and to avoid all insignificant streams, the latter for simplicity of the model. Ideally, an LCA consists of all four stages including raw materials acquisition, manufacturing, use and waste management. Some studies use this approach which is called cradle-to-grave [7, 9, 11, 13-15, 21-25, 30, 31] and others use the cradle-to-gate approach [2, 3, 6, 8, 16, 26, 32]. It is also suggested another approach which is the allocation of boundaries between the system analysis, the foreground system, and the background system (Indirect effects). This approach have not been used in the reviewed LCAs for ethanol production[8].

Using cradle-to-grave boundary in ethanol production analysis leads to a holistic view of environmental impacts but the choice of the cradle-to-gate seems more appropriate because ethanol is used mostly as fuel. As a result, the environmental performance of the end-use of ethanol in all cases is the same and the differences between the LCA results in ethanol production by using various pathways arise from the raw materials to the end of production. Besides, cradle-to-gate gives the opportunity to point out the hot spots of ethanol production phase when we end the analysis at the end of ethanol production. [2].

D.3.2. Environmental impacts

Another methodological choice in an LCA study is the set of environmental impact category. Different LCAs do not follow the same methodology in selecting the midpoint (impact category) or endpoint (damage category) level. The selection of these different levels arise dissimilarities in the results [2, 7, 9, 27]. Midpoint methods restrict modeling to relatively early stages in the cause-effect chain to limit uncertainties. Endpoint oriented methods model the cause-effect chain up to the end and sometimes they include high uncertainties [33] . Both midpoint and endpoint level indicators have complimentary metrics and limitations. Generally, decision can be made using the midpoint approach which is more certain. But sometimes, it has lower relevance for decision making. In these cases, endpoint indicators can be used which have higher relevance but more uncertainties [34]. For example, it is not obvious which toxicological effects taken into consideration in endpoint level or which assumptions are made for the associated chemical fate. Most of the ethanol LCAs use the midpoint level to show the transparency of their studies.

Figure D.1 shows the breakdown of LCA studies based on the considered environmental impact categories. Generally global warming, acidification, eutrophication and energy used are most often selected metrics for environmental evaluations.

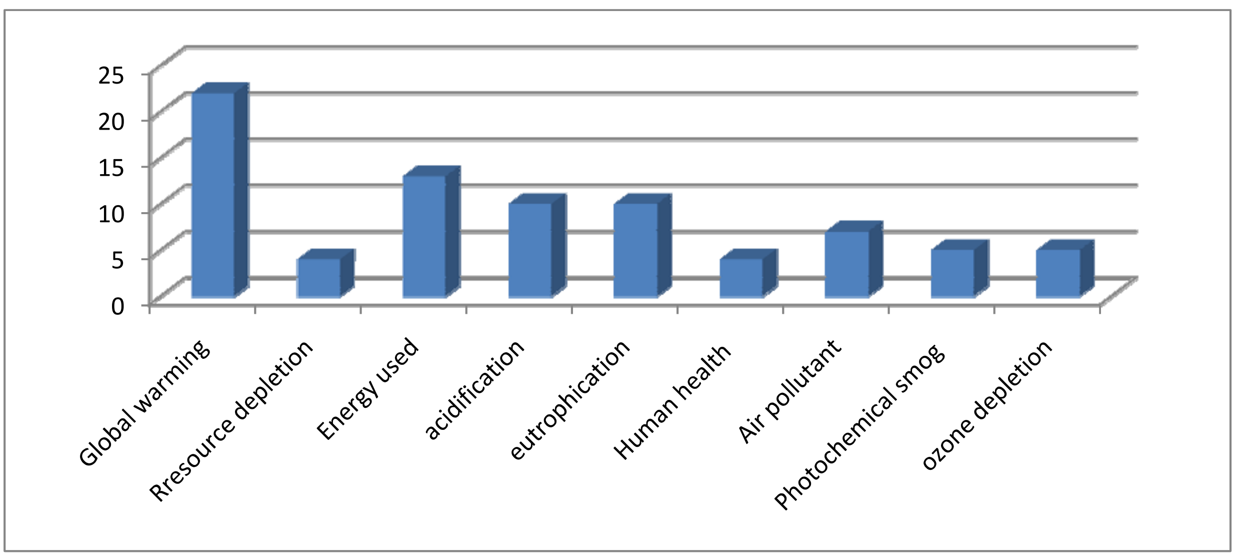

Figure D.1. Breakdown of LCA studies by field of used environmental impact categories

As it is shown, global warming is the most used impact category in reviewed ethanol LCAs. There are different ways of calculation for this impact. Some studies use carbon dioxide (CO_2), nitrous oxide (N_2O), and methane (CH_4) emissions for calculation of GHGs [11, 18, 20]. And some others calculate this impact category only based on CO_2 emission [6, 16, 25, 26]. After global warming category, energy assessment is mostly used for ethanol environmental evaluation. It does not have a common characterisation factor but it is seen as an environmental impact category. The calculation of energy used for process in reviewed studies is based on either energy content [10, 29] or energy consumed [13, 18, 35]. Acidification and eutrophication are both also used in ten LCA studies out of twenty six. The impacts of acidification and eutrophication are mostly related to the use of nitrogen (and phosphorus) in the agricultural processes such as feedstock cultivation.

D.3.3. Allocation

Another key point in LCA studies is the allocation procedure. This is the selection of which share of the environmental burdens of the activity should be allocated to ethanol and other co-products. According to the feedstock used in the process, various co-products are formed. For example, in the sugar cane-to-ethanol process, bagasse (fibre residue from extraction of sugarcane juice) is a co-product which can be used for electricity production. The types of co-products during corn-to-ethanol production depend on the milling system. In the case of wet milling process, corn syrup, corn oil, corn gluten meal, corn gluten feed and food-related products such as vitamins and amino acids can be produced. When dry milling process is used, animal feeds (distillers grains and soluble, DGS) are the potential co-products. For cellulosic feedstocks, electricity is the most common co-product of ethanol [3, 9, 36-38].

The choice of allocation procedure affects the results of LCA considerably. There are different calculation methods for dealing with multiple-product processes. According to ISO standard "The allocation should be avoided by dividing the unit process into two or more sub-processes or expanding the product system to include the additional functions related to co-products. Where allocation cannot be avoided, the inputs and outputs of the system should be partitioned between the different products or functions in a way that reflects the underlying physical relationships or other relationships between them." [39]

Avoiding allocation has different concepts such as system expansion, replacement and substitution. Among the reviewed LCAs, some used system expansion for avoiding allocation and some applied replacement concept in their studies [19, 29]. But these concepts cannot be distinguished firmly in practice so they are regarded as the same method in principle. As a result, all of them are categorized in avoiding allocation method. Two other groups are physical and economical methods. Each of these methods has their advantages and disadvantages which are studied in the following. In the reviewed LCA publications, different allocation methods or all of them are chosen under specific conditions and assumptions in different studies. This is shown in Figure D.2.

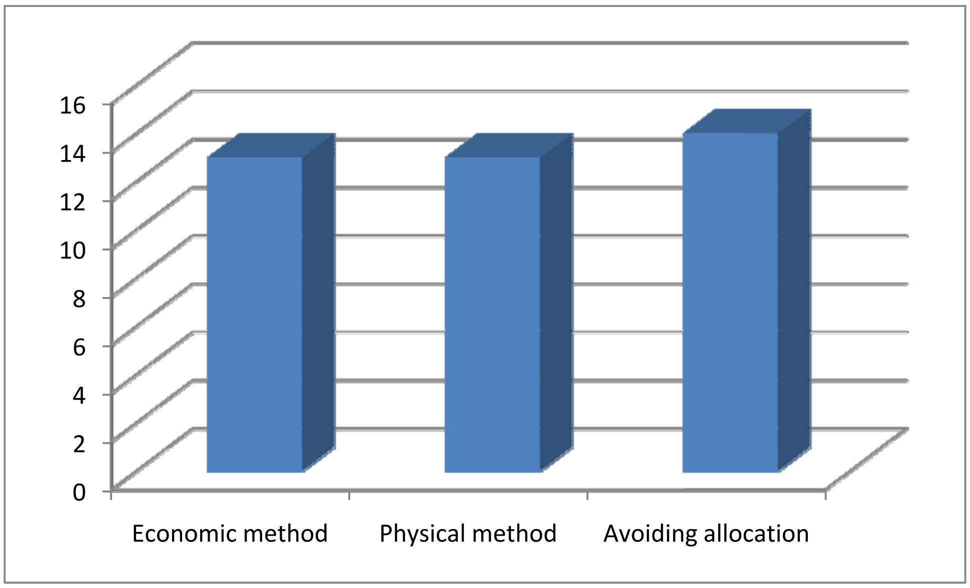

Figure D.2. Varity of different allocation methods

According to Ekvall and Finnveden [2001], avoiding allocation procedure gives the chance to expand the system and model the indirect activities [39]. This method can be also a good alternative when there is not reliable inventory data for products or when the market is restricted[40]. But in the other hand, the appropriate results will be accessible when appropriate data for the indirect effects and functions are used [39]. When avoiding method is used, choosing the substitution products for co-products in the system should be as close to reality as possible in order to have the same environmental burdens. For example DDGS is a co-product of ethanol production through dry milling process. In avoiding method, we need to identify a product which can be replaced by DDGS in order to estimate the environmental impacts of ethanol production. These substitution products are selected differently in different studies such as soybean meal [35], soybean oil[8] or corn/soybean meal[19]. So even with the same avoiding allocation method, results can be different based on the various assumptions or calculation method. As a result, using system expansion is complicated and time consuming as it is necessary to collect accurate data for every sub-process in the system. But on the other hand, it includes all activities and there is no need to divide the impacts among different products.

Physical allocation can be divided into mass and energy-based methods. Mass allocation method mostly gives results but it is not always reasonable. For example assigning the majority of environmental impacts to the co-product which can be used somewhere else is not logical [24]. It cannot be also used for energy output in the system and it seems that simple mass allocation is not a good approach when the quantity of one co-product is far from another. Two different energy-based concepts were used in published LCAs including energy value [2, 8, 15] and energy consumed [41]. Generally physical allocation works well always when there is a close correlation between the physical property of product and co-products [3, 6, 26, 32]. Another advantage is that it is independent of time.

In market value allocation the timeframe of the prices change the results of the assessments. And there is not one single method to monitor the influence and this uncertainty in the system. For example, when economic method is used for ethanol (main product) and animal feed (co-product), the price as the basic data for calculation is changing over time. Börjesson [2009] suggested using a data interval reflecting potential variation in prices as a solution[40].

Generally, selection between two allocation methods, physical and economic, is highly depended on the type of feedstocks used for ethanol production. For example, when we are looking at ethanol production from grains, the energy content of straw is more than the energy content of ethanol but the economic value of straw is 10-15% of this value of ethanol. Nguyen and Gheewala [2008] have also the same discussion when comparing cassava-based ethanol and gasoline. Although gasoline has higher energy content but its octane value is lower than that of ethanol. Consequently, it has less efficient thermodynamic operation in engines. This is the reason why they chose economy allocation method to assess their study [42]. It is argued that economic allocation should be used in the systems with huge quantities of co-products with low economic value.

Some of LCAs avoid allocation procedure or use either economic or physical methods to show the influences of each of them for the final results [2, 12, 15, 17, 20, 24, 29]. According to Kim [2002], sensitivity analysis for ethanol production shows that choosing allocation methods have the most influences on the results in comparison with any other parameters in ethanol production. It is shown that the difference in the net ethanol energy is changed around 30% by choosing different allocation procedures [8]. Malca and Freire [2006] also show in their study that results of LCA for wheat and sugar beet based-ethanol is highly sensitive to the allocation method [2]. The difference of energy renewability efficiency varies more than 50% for wheat based-ethanol. The same result is concluded in the study done by Bernesson et al. [2006]. It is argued that the results are dependent on the allocation method of the environmental burdens between ethanol and by-product [15]. The other LCA study done by Hill, Nelson et al. [2006] introduce Net Energy Balance ratio (NBE, energy output/energy input) for the sensitivity analysis. This ratio is changed from 1.21 in economic allocation to 1.71 in physical allocation (energy content) for corn based-ethanol production with alternative co-products [19].

Although allocation methods are divided into specific categories, each allocation method has been applied differently by various practitioners. In other words, different assumptions and calculation methods can be applied which result the different outcomes even with the same allocation method.

There is a lack of explanation what the key factors are for selecting methodological choices in every situation. It is not logical to identify one single method for it as these choices are highly dependent on the case study and the assumptions which are employed in the study. As a result, selection of the most appropriate methodological choices should be done based on a case.

D.4. Objectives

The objectives of this paper are: a) to assess a body of knowledge related to LCA studies of ethanol production from different feedstocks in order to identify some of the methodological choices that have been made; and b) to evaluate the consequences of methodological choices for ethanol production in order to propose an appropriate LCA methodology

D.5. Methodology

As explained in the literature review, this paper focuses on a survey of 26 LCA studies concerning the production of ethanol from different first and second generation feedstocks. A critical review of the strengths and weaknesses of different approaches was done to determine the methodological choices in an LCA study. In order to propose the most appropriate methodology for ethanol production the following section are assessed.

D.5.1. Characterization of methodological choices

It is known that methodological choices including system boundary, set of environmental impacts and allocation procedure should be made in relation to the goal and scope of the study.

These selections in LCA are relevant to different applications. To assess the performance of these different methodological choices, a base case was defined. This case was selected among the reviewed articles. It enables us to characterize the methodological choices according to the base case and compare different methods and their consequences in the results. By interpretation of different results, the most appropriate methodology for ethanol production in a specific case study is proposed.

D.5.1.1. Exploration of the methodological choices

As mentioned, one life cycle assessment case study was selected from literature review. This study was done by Kemppainen et al. [2005] [3] and the model used in this study was developed based on the mass and energy balances done by National Renewable Energy Laboratory (NREL) [43].

This ethanol production process includes dilute acid prehydrolysis, simultaneous saccharification and fermentation and cellulase enzyme production sections. It begins by feed handling section, where the chips are washed and reduced in size. Then hemicellulose sugars are released by using dilute acid hydrolysis in pre-treatment area and the hydrolazate stream is split to the fermentation step. The cellulase enzymes are produced in cellulase enzyme production area and sent to fermentation reactors for ethanol production. The produced ethanol is purified by distillation and stored in the storage area. There is also waste water treatment section in order to treat the bottom streams of distillations. The recovered water is recycled back to the process and the solid from waste water treatment process and produced biogas are burned in a combustor in order to provide the steam and electricity needed in the plant. In other words, this process is energy self-sufficient and the excess electricity is sent for sale to the grid [3].

In this study the assumed feedstock is timber which was used in the LCA study by Kemppainen et al. [2005] and no change in the mass and energy balance (NREL simulation result) is considered. The components of timber feedstock for the ethanol process are shown in Table D.2.

Table D.2. Composition of feedstock for ethanol process from LCA study by Kemmpainen et al. [4]

Component	% Dry wt basis
cellulose	49.15
xylan	16.89
arabinan	1.04
mannan	3.76
galactan	1.01
acetate	3.38
lignin	24.45
ash	0.31
moisture	68.4

The feed rate of 83333 kg/h of dry biomass is assumed. This amount of feedstock is supposed to be sufficient for production of 60 million gallons of ethanol per year.

Data in this study were collected from a variety of sources including literature, reports and some directly from the used tool SimaPro 7.1, Ecoinvent inventory database. The Life Cycle Inventory Assessment (LCIA) method that was used is impact 2002+. Other data on transport, ethanol process and electricity production are obtained from NREL report [43].

Mass and energy inputs and outputs as shown in Table D.3, were quantified for each step of the process and were manually input into SimaPro to estimate the environmental impacts of the timber-to-ethanol process.

Table D.3. Mass and energy balances

Environmental flows	Input (Kg/hr)
Biomass	83333.00
H_2SO_4	1,839
Hydrated Lime	693
NH_3	1,194
Ammonium sulphate	108
Gasoline	938
Antifoam	268
Diesel	470
Calcium phosphate	108
Environmental flows	**Output (Kg/hr)**
Gypsum (Waste stream)	2433
Ash(Waste stream)	1106
CO_2	117885
Biogas methane	17

D.5.1.2. Application of LCA methodology

The first step of each LCA study, definition of goal and scope, is defined as "to evaluate the environmental performance of timber-to-ethanol production based on an appropriated LCA methodology selected by studying the consequences of different methodological choices".

To access this goal, various selections are applied in the base case and characterized as following:

a. System boundary

As mentioned before, the system boundary should include all important activities under the terms of the goal and scope of the study.

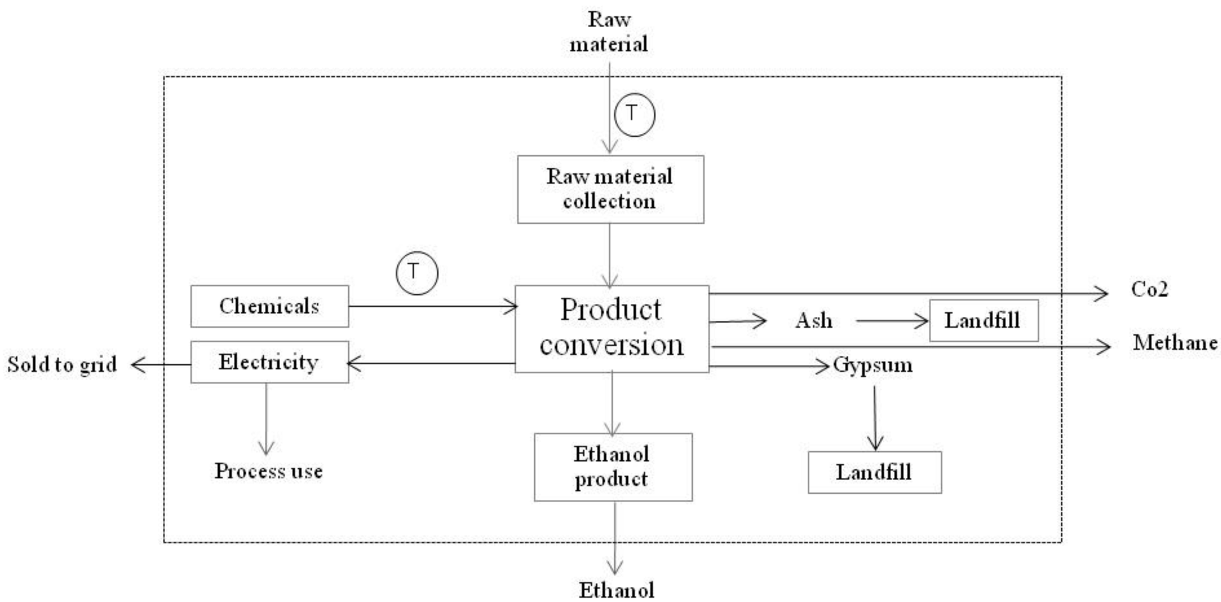

Figure D. 3. System boundary and flows for the overall LCA

As shown in simplified representation, the boundary was expanded to include all activities that would be affected by a change in the system. It starts with the cultivation of raw material, transportation to the mill, conversion of raw material to ethanol and finally ethanol production. The treatment of wastes, the production of chemicals and electricity needed for the process are also accounted in the system. The consequences of including or excluding the end-use of ethanol to the analysis need to be addressed.

The end-use combustion phase in vehicle can be excluded from the boundary as it has always the same environmental impact. The selection of cradle-to-gate increases the chance to describe a status-quo situation and environmental hot-spot identification in order to recognize a number of improvement options. Moreover, the selected boundary shown in the simplified representation is also appropriate when comparing ethanol production from different feedstocks as the end-use of all these pathways is using ethanol as fuel. As a result, cradle-to-gate is selected as the suitable system boundary of our model.

b. Environmental impact category

As mentioned before, the terms of midpoint and endpoint refer to the level of relevancy and uncertainty. In order to select the most appropriate set of environmental indicators, we applied two different methods in the base case. These methods are summarized in the following table.

Table D. 4. Characterization of environmental impact category

Methodological choices	Method I		Method II	
System boundary	Cradle-to-gate		Cradle-to-gate	
Environmental impact category	End point (Damage category)	Human health, Ecosystem quality, Climate change, Resources	Midpoint (Impact category)	Human toxicity, respiratory effects, ionizing radiation, ozone layer depletion, photochemical oxidation, aquatic ecotoxicity, terrestrial ecotoxicity, terrestrial acidification, aquatic acidification, aquatic eutrophication, land occupation, global warming, non-renewable energy, mineral extraction

Both methods have the same system boundary which is cradle-to-gate. The reason of this selection is discussed in the previous section. This enables us to characterize the consequences of different environmental impact categories (endpoint vs. midpoint) on the result when other methodological choices are kept same.

By applying method I and II in the base case, the following results are obtained as shown in the Figure D. 4 and Figure D. 5.

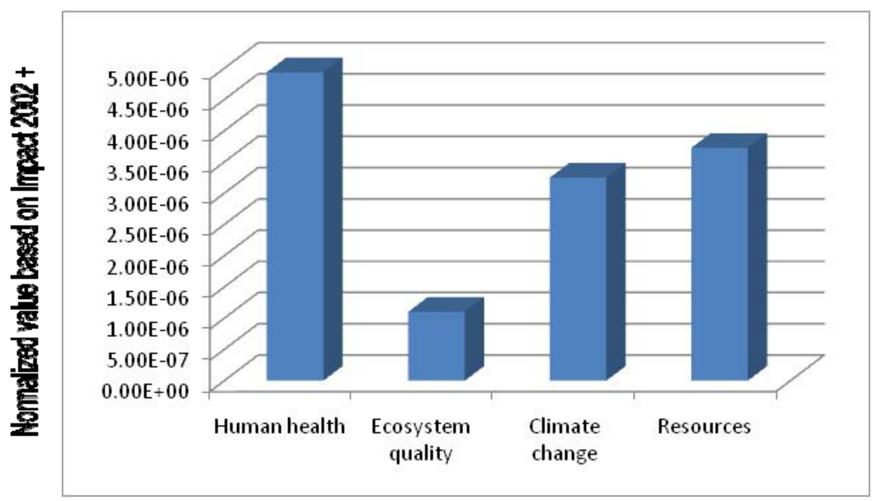

Figure D. 4. Damage category (Endpoint)

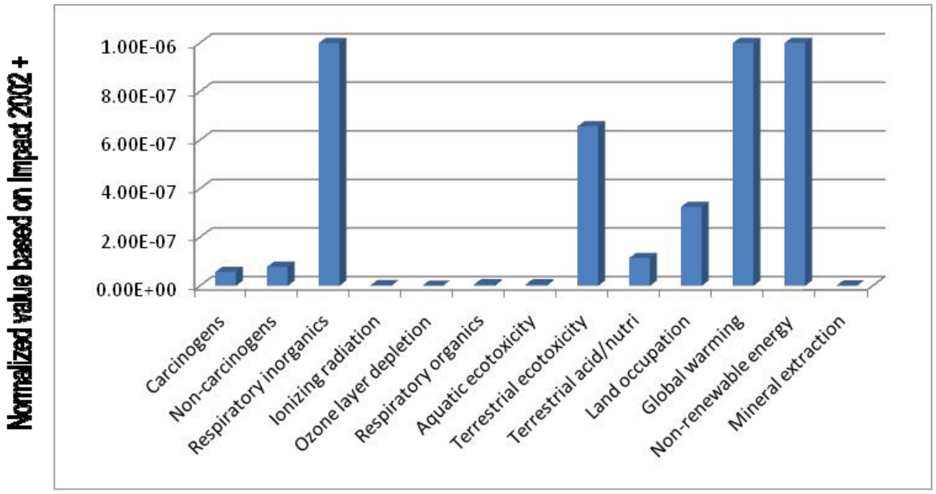

Figure D. 5. Impact category (Midpoint)

It is a general discussion that endpoint level is more understandable. But on the other hand, it is not obvious which effects or assumptions are taken into consideration in endpoint level. This decreases the transparency of the LCA study. For example, ecosystem quality (Figure D. 4) is caused by aquatic and terrestrial acidification, ecotoxicity and land use (Figure D. 5). But it is not clear which of these impacts are brought into the account when the results are presented in endpoint level. This arise more uncertainties in the study. Besides, the midpoint impacts are taken directly from the inventory and they are determined over a certain area. This lack of this transparency in results leads us to select the midpoint level as an appropriate environmental category for this base case.

c. Allocation procedure

As discussed before, allocation procedure is one of the key points which bring uncertainty into the assessment when there is more than one product in the system. Following the ISO guideline, avoiding allocation is selected in the first step in order to assess its consequences on the results. If the avoiding allocation is not applicable, environmental impacts should be divided between ethanol and electricity based on the physical or other relationships. In order to characterize and determine a better method, both system boundary and environmental impact category are fixed for the systems and two allocation procedures are applied. Table D. 5 shows the methodological choices selected for the study by two methods.

Table D. 5. Characterization of allocation procedure

Methodological choices	Method I	Method II
System boundary	Cradle-to-gate	Cradle-to-gate
Environmental impact category	Midpoint (Impact category)	Midpoint (Impact category)
Allocation procedure	Avoiding allocation	Physical allocation

In method I, the system boundaries and the functional unit were expanded to include all the activities related to both products (ethanol and electricity). In method II, environmental impacts of the whole system are divided between ethanol and electricity based on the energy content. The results of two methods are shown in the Figure D. 6.

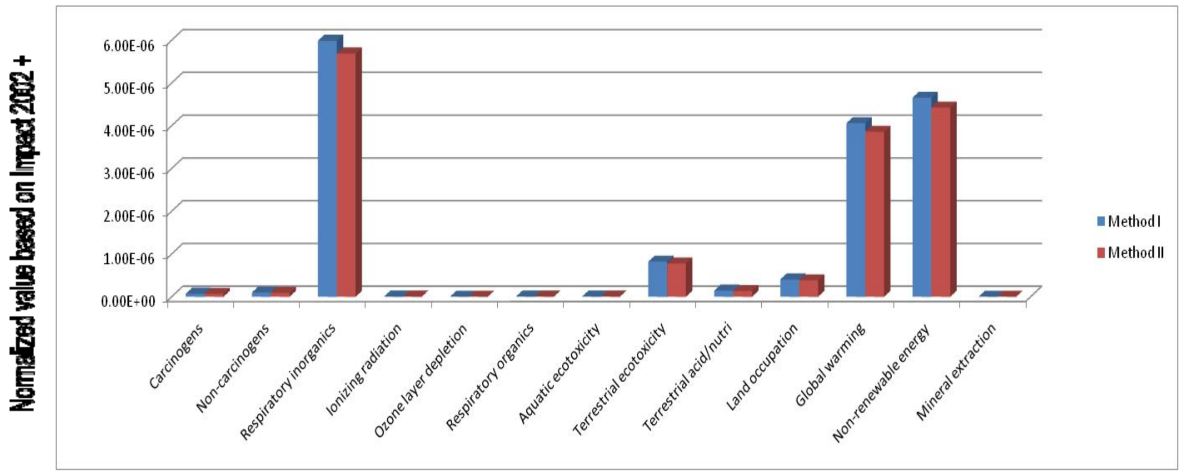

Figure D. 6. Characterization of allocation procedure

According to the figure, the amounts of environmental impacts from method II (physical allocation) are lower than those from method I (System expansion). This difference is obtained because of the partitioning and distribution of environmental impacts between ethanol and electricity. This value for allocation can be different based on the different assumptions used by analyzers. As a result, to avoid this uncertainty, it is suggested to avoid allocation in order to have the overall emissions of the whole system which is also suggested by ISO as the first option in this kind of problems. In this method all activities are also accounted for in the model and it is closer to the reality. As a result, avoiding allocation is selected for this study.

D.5.1.3. Results and discussion

According to characterization of methodological choices in the previous sections, the most appropriated method for this specific study of timber-to-ethanol production is selected and summarized in the following table.

Table D. 6. Selected methodological choices for the specific base case of ethanol production

Methodology	Selected method
Goal	To compare the environmental impacts of ethanol production from upper Michigan timber based on the most appropriate LCA methodological choices
System boundaries	Cradle-to-gate
Functional unit	1 MJ of ethanol + 2.3*10e-3 MJ of electricity
Allocation approach	Avoiding allocation/ System expansion
Environmental impact indicators	Human toxicity, respiratory effects, ionizing radiation, ozone layer depletion, photochemical oxidation, aquatic ecotoxicity, terrestrial ecotoxicity, terrestrial acidification/nutrification, aquatic acidification, aquatic eutrophication, land occupation, global warming, non-renewable energy, mineral extraction
LCIA method	Impact 2002 +

While the selection of the methodological choices will affect the results because of the fundamental differences in modeling, the choice of a normalization reference aims at better interpreting the results, which is critical if LCA is to be used for practical decision-making. Normalization should be applied in order to determine which environmental impact is more significant in ethanol production. The normalization approach should fulfill the horizon of the study. Norris [44] discussed the internal and the external approaches for normalization in LCIA. In internal approaches, the score of a particular category is divided by a function of the values obtained for the studied alternatives for that category. External approaches are generally linked with the contextual view in which the relative significance of results in different impact categories is assessed. External normalization allows the evaluation of the relative significance of a category's result to the global impact of a chosen referential system. This system should be justified based on the geographical location and the technical characteristics of installation. As sugar and starch for ethanol have been until now the primary raw materials, the technology for first generation of ethanol production is well known. In order to make a good judgment between different types of feedstocks for ethanol production, in our case woodchips-to-ethanol, the corn-to-ethanol process is selected as the reference system. This enables us to compare the environmental impacts of a second generation ethanol with the impacts of the first generation process.

Based to this approach, the significance of environmental impacts can be calculated according to the following equation where Ni is the normalized environmental performance, Ii,case is the characterization results for timber-to-ethanol production and Ii,RS is the characterization results of reference system.

$$Ni = \frac{Ii,case - Ii,RS}{Ii,case} \qquad (Equation\ 1)$$

In this approach, change is compared to the total improvement when implementing the corn-to-ethanol production as reference system. This difference is divided by the initial performance of the system. A positive result means that the alternative performs worse than the reference system, while a negative result means that it performs better.

The results of external normalization are shown in the following graph.

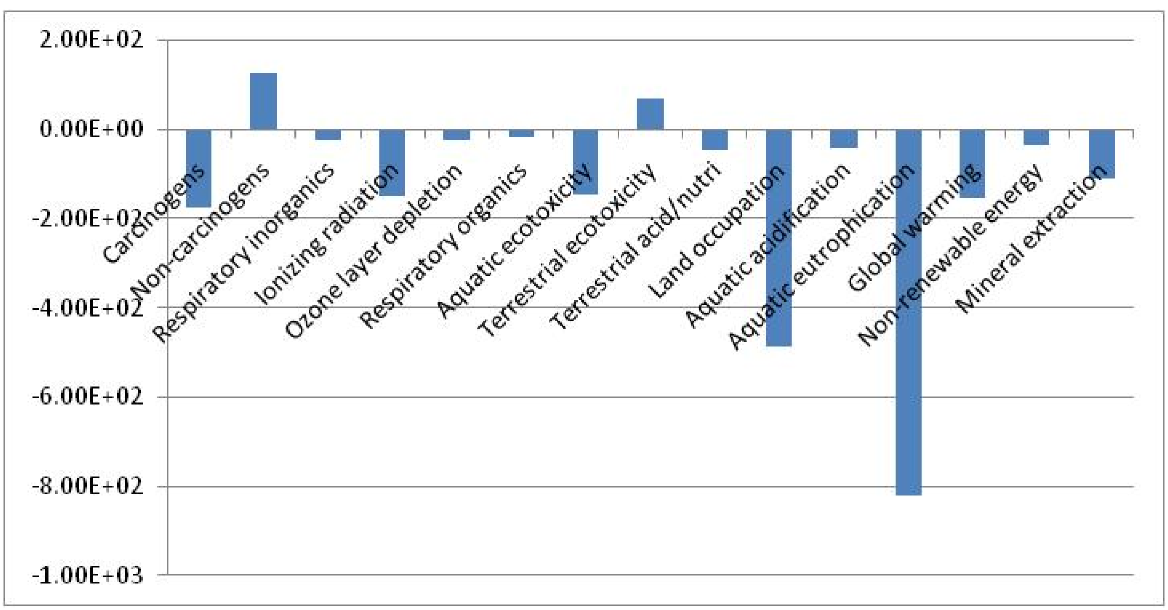

Figure D.7. Normalized environmental indices for the timber-to-ethanol production

As it is shown, the production of ethanol from timber has a better environmental performance in most of the impact categories. For example, the obtained result for eutrophication shows a very good environmental advancement when ethanol is produced from timber in comparison with corn-based ethanol. This is mainly result of emissions associated with corn cultivation. Land use and aquatic ecotoxicity are two other categories with more environmental friendly impacts for timber-to–ethanol, based on the external normalization method. In terms of land use impact, farming of first generation feedstock for ethanol production define environmental performance of the woodchips to ethanol better, when there is no need of using fertilizers and pesticides for second generation ethanol.

Only two impact categories, non-carcinogens and terrestrial ecotoxicity impacts, show worse environmental performance for wood-to-ethanol case. These impacts refer to the impact of heavy metals specifically Zinc and Copper emitted to the soil and air ecosystem. According to the Ecoinvet report, these are listed as emissions from combustion using diesel and petrol in the process and their main significant effects are associated with terrestrial ecotoxicity and non-carcinogens[45]. Howcome this is the case for wood-to-ethanol as te process is energy self-sufficient, meaning that no fossil fuels are needed in the process? Are the emissions from transportation, because, as you mention, the wood raw material does not need cultivation which would be also a consumer of fossil fuels?

Based on the methodological choices and normalized method selected in this paper, the conversion of woodchips-to-ethanol is a potential fuel for transportation according to environmental evaluation metrics. These metrics include global warming, acidification/Eutrophication and land occupation which have lower environmental impact compared to corn-to-ethanol case.

D.6. Conclusions

Generally the methodological choices (system boundaries, allocation procedure and environmental impact categories) are key points for an ethanol LCA study. It is obvious that there are trade-offs when selecting the most appropriate methodology for an ethanol LCA. These different methodological selections compromise poses a challenge for LCA analyzer.

The LCA study done by Kemppainen et al [2005] was selected as a base case in order to characterize the methodological choices. The results show that for this specific case, when ethanol is assumed as fuel, cradle-to-gate is an appropriate system boundary to avoid the extra activities in the system. It also gives the opportunity to compare ethanol production from different feedstocks and identify the hot-spots in the system. In terms of environmental impact category, selection of midpoint seems to be more appropriate because of more certainties in this level. The allocation method can have a strong influence on the results among the mentioned key points. In the case of timber-to-ethanol producing electricity as a co-product, the best selection is avoiding allocation by system expansion. It enables to include all activities related to both ethanol and electricity production.

Besides, while environmental impacts are assessed in ethanol production, their importance should be identified. In order to determine which impact is more significant in ethanol production, normalization should be applied. This helps to establish a set of metrics to have a better decision. For this specific case, an external approach of normalization is applied. The approach includes the selection of corn-to-ethanol as a reference system which is a well-known process. It also enables a comparison between the first and second generation ethanol production. The results show that the conversion of timber to ethanol is a potential environmental opportunity when global warming, acidification/eutrophication and land occupation are selected as the evaluation metrics. This result may be different if other metrics are chosen. As a result, selection of the environmental evaluation metrics in order to have a better decision making is essential in an LCA. Additional studies are needed to select the most appropriate environmental screening metrics to evaluate the performance of ethanol from different biomass.

Acknowledgments

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